"REACTIONS OF CHLORINE ATOMS WITH OLEFINES"

By

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To MY FATHER.

PREFACE

The work presented in this thesis was directed primarily towards the study of the kinetics of chlorine atom addition to olefines, using the competitive technique.

In the field of gas phase halogen reactions, the competitive technique had, up to the time of commencement of this work, been applied mainly to hydrogen abstraction reactions. It was hoped that by a simple extension of this method it would be possible to obtain absolute Arrhenius parameters for reactions of the type:-

$$A + Cl. = .ACl \qquad (2)$$

where A is an olefine molecule.

(The chlorine atoms were produced photochemically)

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Abbreviations and Units

Except where otherwise stated the concentration and time units used for A factors and rate constants, throughout this thesis, are moles/litre and seconds, respectively, and activation energies have been given in kilocalories/mole.

For convenience the following abbreviations have been used in chapters 3, 4 and 5, in addition to those explained in the text.

DCE = 1.2 dichloro ethane.

DCP = 1.2 dichloro propane.

DCIB = 1.2 dichloro isobutane.

DMV = dimethyl vinyl chloride.

MA or M allyl Cl = Methallyl chloride.

cis DE or CDE = cis dichloro ethylene.

sPr or sPrCl = secondary propyl chloride.

pPr or pPrCl = primary propyl chloride.

tBuCl = tertiary butyl chloride.

RV = Reaction vessel.

M = Mixture pressure ie olefine + propane.

Symbols placed in round brackets generally denote concentrations.

Except where otherwise stated all pressures are in cm or mm of Mercury.

CONTENTS.

CHAPTER I

INTRODUCTION

1.1. GENERAL HISTORICAL

The purpose of Chemical Kinetics is the elucidation of reaction mechanisms and the determination of the factors which influence the rate and direction of any given reaction; particularly the Arrhenius parameters.

Reactions in the solid, on surfaces and in solution, tend to be complex owing to the indeterminate effect of such factors as solvation and adsorption. It is not therefore unexpected that the greatest advances have been made in the field of homogeneous gas phase reactions. Of these, halogenations, where the reactive entities are likely to be simple, have offered a very fruitful field of study and have made a major contribution to our theoretical understanding of reaction kinetics.

The pioneer work of Bodenstein and co-workers on the photochemical reaction, between Hydrogen and Bromine[1] (1909), and between Hydrogen and Chlorine[2] (1913) opened the door to the present era in gas phase kinetics. The high quantium efficiency of the latter reaction in the absence of oxygen (10^4-10^6) led Bodenstein to propose that an ionic chain mechanism was involved. Subsequent modification of this theory by Nernst[3] (1919), who suggested that the chain was carried by free atoms, led Bodenstein & Unger[4] to put forward their well known and now generally accepted atomic chain mechanism (see page 4).

In 1929 Paneth and co-workers[5] studied the decomposition of certain metal allkyls by passing them down a heated quartz tube. By observing that the decomposition products would remove metallic films placed in the tube at a distance from the heated area they obtained evidence for the existence of free alkyl radicals. Rice & Hertzfeld[6]

in 1934 employed the idea of free radicals to explain the results of studies on the thermal decomposition of hydrocarbons and other simple molecules and shortly afterwards Pease[7], Senenow[8] and others, applied Bodenstein's atomic chain theory to the oxidation of hydrocarbons. They produced a comprehensive theory which involved both hydrocarbon and oxygenated free radicals.

It is now generally agreed that the majority of gas phase reactions take place through the agency of free radicals or free atoms. Direct evidence for the existence of atomic species was obtained as early as 1933 by Rodebush[9] & Klingelhoeffer who showed that free chlorine atoms were produced when an electric discharge was passed through a glass vessel containing gaseous chlorine. However up until quite recent times evidence for the existence of free radicals was only obtained by inference and usually depended upon detailed kinetic studies combined with a rather crude product analysis. The development of flash photolysis and electron spin resonance spectroscopy have now given direct evidence of reactive entities containing unpaired electrons.

Most of the kinetic work before 1940 was carried out using pressure changes to follow the course of reaction. Analytical methods of high sensitivity were not then available and only major reaction products could be determined by such methods as conventional gas analysis, fractional distillation, and volumetric or gravimetric analysis. While analysis for functional groups could be carried out, analysis for different homologues was difficult, if not impossible. As a result of these limitations early investigations were devoted almost entirely to the determination of overall rate expressions and the attempted correlation of these expressions with those obtained on the basis of assumed reaction schemes. Interest in the rates of the individual reaction steps was aroused in the late

1930s by the development of Eyring's transition state theory[10], which provided a method of predicting the Arrhenius parameters for elementary reactions. The much more detailed investigations necessary for determining the rates of these reactions were not possible until after 1943 when the introduction of such techniques as IR spectroscopy, mass spectrometry[11] (1945) and more recently gas chromatography[12] (1955), provided accurate methods for the microanalysis of reaction products. Application of these analytical methods to gas kinetics problems has been so successful that at the present time the accuracy with which Arrhenius parameters for elementary reactions can be obtained by experiment, is far in advance of any of the available theoretical predictions.

1.2. REACTION MECHANISMS

Chlorination of Hydrogen:- As we have already seen the first photochemical chlorination study of any significance was that made by Bodenstein using hydrogen as reactant. In the years following up to 1940 several hundred further investigations of this system were carried out, which, whilst they produced virtually no change in the originally proposed mechanism, were largely responsible for the advance of kinetic methods of investigation and general vacuum techniques. The extremely long chains, characteristic of this type of reaction, caused it to be very sensitive to the presence of impurities, particularly oxygen, and many results of a contradicting nature were obtained. Coehn & Jung's[13] report that, in the complete absence of water no reaction took place in visible light, vied with that of Bodenstein & Dux[2] who claimed photochemical combination even for an intensively dried mixture, and furthermore noticed no effect on adding up to 10mm of water vapour. As a result of work by Kistiakowsky[14] it was later concluded that the inhibition was due to preferential removal of chlorine atoms by some impurity introduced in the drying process.

Bodenstein & Unger's[4] mechanism for the oxygen free reaction involved the following steps:

Initiation		$Cl_2 + h\nu = 2Cl\cdot$	(1)
Propagation	{	$Cl\cdot + H_2 = HCl + H\cdot$	(2')
	{	$H\cdot + Cl_2 = HCl + Cl\cdot$	(3') *
Inhibition		$H\cdot + HCl = H_2 + Cl\cdot$	(-2')
Termination	{	$Cl\cdot + Y = ClY$	(7')
	{	$H\cdot + Y = HY$	(8')

where Y could be the reaction-vessel wall or some volatile compound of silicon.

Initiation was achieved by irradiation with light of wave

* See Appendix A for complete mechanism.

length in the continuous region of the chlorine spectrum i.e. 4785A or less.

No evidence for inhibition by HCl (reaction (-2') was obtained and chain termination was assumed to be mainly by (7'). Application of the now standard, stationary state approximation to chlorine and hydrogen atoms yields the expression:-

$$R_{HCl} = \frac{4k_2' I_{abs}(H_2)}{k_7'(Y)}$$

for the overall rate of production of HCl. This corresponds with the experimentally determined rate equation

$$R_{HCl} = kI_{abs}(H_2),$$

provided (Y) can be considered constant. If Y is the wall, (7') can be regarded as leading to first order recombination of chlorine atoms thus:-

$$Cl\cdot + Wall = \tfrac{1}{2}Cl_2$$

and (Y) no longer enters the theoretical rate expression.

Whereas Bodenstein had shown termination to be first order in chlorine atom concentration, other workers[15] using higher pressures obtained a rate equation of the form:

$$R_{HCl} = kI_{abs}^{\frac{1}{2}}(H_2)$$

Termination was thus now second order.

Possible second order termination steps are:

$$H\cdot + H\cdot + M = H_2 + M \qquad (4")$$

$$H\cdot + Cl\cdot + M = HCl + M \qquad (5")$$

$$Cl\cdot + Cl\cdot + M = Cl_2 + M \qquad (6)$$

where M is a third body and is required to remove excess energy. Termination was thought to be mainly by reaction (6), in which case it can be shown that

$$k = 2^{\frac{1}{2}}k_2'/k_6^{\frac{1}{2}}(M)$$

In the light of present knowledge the following justification can be made for the predominance of reaction (6). The activation energy for reaction (3')

$$\Delta H_3' = -45{\cdot}1 \text{ k. cal.}$$

is much less than that for reaction (2')

$$\Delta H_2' = 1{\cdot}1 \text{ k. cal.}$$

and thus any hydrogen atoms produced will be immediately removed by reaction with chlorine molecules. Termination step (4") can therefore be disregarded. Both (5") and (6) are termolecular and as the hydrogen atom concentration will be very small (6) is the only significant termination step. This change to second order termination at high pressures is partly due to less diffusion of chlorine atoms to the walls but is also due to an increased chlorine atom concentration which enhances the rate of homogenous termination by

$$Cl\cdot + Cl\cdot + M = Cl_2 + M$$

thus reduces the chain length.

It can be readily seen that the gradient of the line obtained when the temperature dependence of the overall rate constant is interpreted in the form of the Arrhenius equation, will give a measure of

$$E_2 - E_7, \text{ or } E_2 - \tfrac{1}{2}E_6$$

depending on whether the system is studied at low or high pressures. Both E_7, and E_6 are likely to be small and have commonly been assumed equal to zero. Making this assumption Hertel[17], working at room temperature obtained

$$E_2 = 5800 \pm 1000 \text{ cal.}$$

whilst Potts & Rollefson[18] obtained values of

E_2 of 4500 ± 1000 cal. below 170°K. and

5800 ± 1000 cal. above 200°K.

Whilst these values are only approximations the true value of E_2 can

reasonably be expected to lie in the range 4500 - 6000 cal.

Chlorination of Alkanes:- The gas phase chlorinations of alkanes exhibit the usual characteristics of free radical chain reactions. As a result of the very long chains involved it has not been possible to formulate the reaction mechanisms precisely but it seems likely that they will be analogous to those for the chlorinated alkanes (see next section) and hydrogen.

The photochemical chlorination of an alkane RH can thus be represented by the following steps:

$$Cl_2 + h\nu = 2Cl\cdot \qquad (1)$$

$$Cl\cdot + RH = R\cdot + HCl \qquad (2')$$

$$R\cdot + Cl_2 = Cl\cdot + RCl \qquad (3')$$

$$R\cdot + HCl = Cl\cdot + RH \qquad (-2')$$

$$Cl\cdot + RCl = R\cdot + Cl_2 \qquad (-3')$$

$$R\cdot + R\cdot = R_2 \qquad (4')$$

$$R\cdot + Cl\cdot = RCl \qquad (5')$$

$$M + Cl\cdot + Cl\cdot = Cl_2 + M \qquad (6)$$

Wall termination has been neglected in this scheme though it may still be important at sufficiently low pressures.

The termination steps (4') and (5') though similar to (4") and (5") of the hydrogen scheme, are no longer termolecular; they are therefore likely to be more important than (6). In fact steps (4'), (5') and (6) can all be significant in alkane chlorinations, their relative importance varying with reaction conditions.

Further understanding of the reaction mechanisms can be obtained by studying the relevant thermochemistry. The bond strengths D(H -Cl) and D(Cl -Cl) are 102.2[16] and 57.07 k.cal. respectively whilst

common values for D(R -Cl) and D(R -H) are around 81, and 90-100 k.cal. The chain carrying steps (2') and (3') are therefore exothermic and the resultant low activation energies make these steps very fast. By similar reasoning inhibition by reactions (-2') and (-3') is negligible, and the chains are therefore very long. A chain length of 10^7 has been obtained for the thermal reaction with propane[19].

When termination steps (4') and (5') predominate, the rate equation obtained by the stationary state method neglecting (-2') & (-3') is:-

$$R_{RCl} = \frac{(2I_{abs})^{\frac{1}{2}} k_3'(Cl_2)}{\left[k_3'k_5'(Cl_2)/k_2'RH + k_4\right]^{\frac{1}{2}}}$$

Chlorination of Substituted Alkanes:- Although quite a large amount of work has been done on the chlorination of chloro-alkanes, particularly chloroform, only the work of Goldfinger et al. has thrown much light on the reaction mechanisms involved.

Several studies[20, 21] were carried out on the photochlorination of pentachloroethane and tetrachloroethylene. As only one hydrogen atom is available for abstraction in C_2HCl_5 secondary chlorination cannot take place and the system is relatively simple.

C_2HCl_5 and C_2Cl_4 were chlorinated separately and also competitively, and the following general mechanism was suggested for both reactions[22]:

$$Cl_2 = 2Cl\cdot$$

$$Cl\cdot + C_2Cl_4 = C_2Cl_5\cdot \quad (2) \qquad Cl\cdot + C_2HCl_5 = \cdot C_2Cl_5 + HCl \quad (2')$$

$$\cdot C_2Cl_5 + Cl_2 = C_2Cl_6 + Cl\cdot \quad (3 \text{ or } 3')$$

$$\cdot C_2Cl_5 = Cl\cdot + C_2Cl_4 \quad (-2) \qquad \cdot C_2Cl_5 + HCl = Cl\cdot + C_2HCl_5 \quad (-2')$$

$$C_2Cl_6 + Cl\cdot = \cdot C_2Cl_5 + Cl_2 \quad (-3 \text{ or } -3')$$

$$\cdot C_2Cl_5 + \cdot C_2Cl_5 = C_2Cl_6 + C_2Cl_4 \text{ or } C_4Cl_{10} \quad (4 \text{ or } 4')$$

$$\cdot Cl + C_2Cl_5 = C_2Cl_6 \qquad (5 \text{ or } 5')$$

$$2Cl\cdot + M = Cl_2 + M \qquad (6)$$

By interpretation of both the separate and competitive systems in terms of complex stationary state equations, assuming (-2'), (-3') and (6) negligible they were able to obtain values for several complex rate constant ratios.

Values of $k_3/k_4^{\frac{1}{2}}$ obtained from the C_2HCl_5 system at 363° and 373°K were found to lie precisely on the plot of log $k_3/k_4^{\frac{1}{2}}$ v 1/T obtained from the C_2Cl_4 system between 358° and 450°K. Furthermore they obtained k_3 between 360° and 520°K by a combination of results of the rotating sector studies on both systems, and from the C_2Cl_4 system in steady light obtained the temperature dependence of $k_3(k_2/k_5k_{-2})^{\frac{1}{2}}$.

These results allowed the calculation of Arrhenius parameters for k_4 and k_5k_{-2}/k_2 which showed excellent agreement with the corresponding values obtained directly from rotating sector studies on the C_2Cl_4 system.

Several other rate constant cross checks of this nature were made with the competitive reactions of C_2Cl_4 with C_2HCl_5 and other chloromethanes.[23]

In general good agreement was found between the values obtained by direct experiment and those obtained indirectly by combination of the results from different experiments. This can be taken as a good indication that the proposed reaction scheme is correct.

Whilst the products of reactions (4) and (5) were not known with certainty they concluded that for the C_2Cl_4 system termination was mainly by (5) up to 430°K but by (4) between 520° and 560°K, whereas for the C_2HCl_5 system both (4) and (5) were equally important below 400°K. For both systems wall termination was believed to be negligible.

Application of the above mechanism to the photochlorination of chloroform[24] was found to explain the observed experimental results if as

before steps (-2'), (-3') and (6) were neglected. The reaction order under initial conditions was found to = 3/2 when the ratio $p(Cl_2)/p(CHCl_3)$ was unity but varied slightly as this ratio was changed. This could be explained by the increase in importance of chain termination by reaction (5) relative to that by (4), as the proportion of chlorine in the initial mixture was increased.

Newton & Rollefson[25] have shown that (-2') does in fact occur to some extent in this system, as they obtained some deuterochloroform on studying the reaction in the presence of deuterium chloride. However it seems that Goldfinger's mechanism gives a good general picture of the reaction and it is certainly superior to that of Schumacher & Wolff[26] who proposed that termination was by

$$2CCl_3^{\cdot} + Cl_2 = 2CCl_4$$

which contradicts the reported formation of reasonable amounts of hexachloroethane.[25]

It should be noted that the above work by Goldfinger et al. not only establishes the mechanism for alkane chlorinations but also at the same time shows that the chlorination of C_2Cl_4 proceeds in an analogous manner. A general scheme for the chlorination of olefines based on this mechanism is given in Appendix A.

Photosynthesis of Phosgene:- Little detailed work on olefine chlorinations had been carried out prior to the above investigation of the C_2Cl_4 system. However several authoritative publications[27, 28, 29] have drawn parallels between the photochloriantion of carbon monoxide and the chlorination of olefine systems, and it seems therefore advisable to consider the mechanism proposed for the phosgene synthesis.

Very many investigations[28] have been made of the CO system. The schools of Bodenstein and of Rollefson[30] in particular disagreed on

the precise reaction mechanism. However further work by Bodenstein[31] and more recently Burns & Dainton[32] has shown the Bodenstein mechanism to give a better correlation with the observed results.

Bodenstein et al. studied the photochemical reaction at room temperature and the thermal reaction between 350° and 450°C. They used the rate of pressure change as their measure of the overall reaction rate and obtained for the photochemical reaction the rate law.

$$R_{COCl_2} = k\, I_{abs}^{\frac{1}{2}} (CO)^{\frac{1}{2}} (Cl_2) \qquad (I)$$

They proposed the following reaction scheme:

$$Cl_2 + h\nu = 2Cl\cdot \qquad (1)$$

$$CO + Cl\cdot = \cdot COCl \qquad (2)$$

Equilibrium

$$\cdot COCl = CO + Cl\cdot \qquad (-2)$$

$$\cdot COCl + Cl_2 = COCl_2 + Cl\cdot \qquad (3)$$

$$\cdot COCl + Cl\cdot = CO + Cl_2 \qquad (5)$$

Assuming that the equilibrium

$$K_{COCl} = \frac{k_{-2}}{k_2} = (CO)(Cl)/(COCl)$$

is maintained, the application of the stationary state treatment to (Cl) and (COCl) yields:

$$R_{COCl_2} = k_3 I_{abs}^{\frac{1}{2}} (CO)^{\frac{1}{2}} (Cl_2) / k_5^{\frac{1}{2}} K_{COCl}^{\frac{1}{2}} \qquad (II)$$

which is the same as the experimental rate law if the constants are equated.

Now the quantium yield $= \gamma = \dfrac{R_{COCl_2}}{I_{abs}}$

$$\therefore \quad k = k_3 / k_5^{\frac{1}{2}} K_{COCl}^{\frac{1}{2}} = R_{COCl_2}^{\frac{1}{2}} \gamma^{\frac{1}{2}} / (Cl_2)(CO)^{\frac{1}{2}} \qquad (III)$$

All the terms on the R.H.S. of the equation III were known and by carrying out experiments at 283° and 313°C they obtained the temperature dependence of Log k. (See next section).

A change in the rate equation[31, 33] at low pressures (below 30 mm)

and high temperatures, to the form

$$R_{COCl_2} = k\ Ia(Cl_2)(CO)$$

was interpreted in terms of wall termination taking precendence over termination by (5).

The low bond strength of CO -Cl

$$D(CO\text{ -}Cl) = 6{\cdot}3 \text{ k. cal.}$$

allows the equilibrium to be easily attained in this system. However as we will see later (p 31) there is now evidence that the corresponding bond strengths D(A -Cl) for the olefine series $C_2H_{4-n}Cl_n$ are all greater than 16 k. cal. and even for the weakest bond namely C_2Cl_4 -Cl equilibrium conditions are not likely to be established below 150°C.

1.3 EVALUATION OF RATE CONSTANTS AND ARRHENIUS PARAMETERS

Old Methods: Ideally for the advancement of scientific understanding theoretical predictions should be capable of direct experimental testing. The very complex nature of the wave mechanical treatment of chemical reactions makes it virtually impossible at the present time to make detailed predictions for any but the simplest type of reaction. It is therefore important to be able to measure the Arrhenius parameters for simple elementary reactions on an absolute scale. Early workers were inhibited from studying such reactions by the lack of sufficiently sensitive methods of analysis but the introduction of modern analytical techniques has brought about the development of accurate methods for determining absolute rate constants. Before dealing with these modern methods we will first consider what information may be obtained from the earlier work.

Most of the early investigations were confined to the determination of accurate overall rate equations. The successful interpretation of the observed overall rate constant then depended on assuming a reaction mechanism which, when treated by the stationary state approximation, would yield a theoretical rate equation of the same form as that observed experimentally. The form of the theoretical expression obtained for photochlorinations is mainly decided by the nature of the chain termination step. When termination can be considered to take place predominantly by only one reaction, then, in very general terms the rate expression may take one of the two forms:

$$\text{a)} \quad K_p I_{abs} K f(c)/K_t$$

$$\text{or} \quad \text{b)} \quad K_p I_{abs}^{\frac{1}{2}} K f(c)/K_t^{\frac{1}{2}}$$

where k_p and k_t are the rate constants for propagation and termination respectively and K may be either a combination of other significant rate

constants, or = 1. f(c) is a concentration term, a) and b) are obtained when termination is predominatly first or second order respectively; k_p may be either k_3 or k_2 depending once again on the termination step. Thus when termination is by first or second order removal of chlorine atoms $k_p = k_2$. However in the majority of cases termination is by second order combination of other chain carriers and k_p then = k_3. Sometimes reaction (-2) is significant as in the $COCl_2$ system and then

$$k \text{ in a) or b)} = k_2/k_{-2}$$

i.e. the equilibrium constant, and

$$k_p = k_3$$

It is therefore apparent that the precise nature of the termination step must be known if meaningful rate constant data are to be obtained from overall rate expressions. In long chain mechanisms the concentration of specific termination products is too small for analysis and usually the main termination step is deduced by comparing the experimental rate equation with theoretical equations based on possible termination steps. Methods of determining rate constants based on overall kinetics are accurate if the reaction mechanism is known with certainty, but where the precise mechanism is in doubt it may be possible to formulate more than one scheme which will fit the observed kinetic expression.

By reference to the section on mechanisms it can be seen that often termination of chains takes place by more than one method (e.g. in alkane chlorination) in which case the overall rate expression is too complex for one to obtain useful rate constant data. However interpretation of the temperature dependencies of the overall rate constant in terms of the usual Arrhenius equation:

$$\text{Log}_{10}k = \text{Log}_{10}A - \frac{E}{2.303RT}$$

may sometimes yield simple activation energy differences. For instance the hydrogen chlorine reaction gave $E_2' - \frac{1}{2}E_6$ or $E_2' - E_7'$ depending on reaction conditions. In such cases it is commonly assumed that the activation energy for recombination of free radicals is zero and thus the overall rate constant ratio gives a value for E_2. However there is very little precise data available on atom or free radical recombinations and the values of E_2 obtained in this way cannot be regarded as accurate. (For iodine

$$I\cdot + I\cdot + M = I_2 + M$$

has a slightly negative activation energy[34] and it seems likely this may also be the case for chlorine atom recombination).

Even when termination can be considered to take place by one predominant method, complications in the reaction mechanism may preclude one from obtaining simple activation energy differences. The phosgene synthesis, where the equilibrium between reactions (2) and (-2) is attained, is a good example of this state of affairs. Thus the temperature dependence of the overall rate constant which Bodenstein[31] obtained for this system could only give values for the complex expressions

$$A_3/A_5^{\frac{1}{2}}A_{COCl}^{\frac{1}{2}} \quad \text{and} \quad E_3 - \tfrac{1}{2}(E_5 - E_{COCl})$$

Whilst these values alone are of little use it can be seen that if any two of k_5, k_3 or K_{COCl} could be obtained absolutely from another source, the remaining k could be calculated.

In principal values for absolute rate constants could be obtained by studying <u>thermal</u> chlorination systems under steady state conditions. For the simplest case, e.g. hydrogen, the overall observed activation energy would be $E_2 + \frac{1}{2}D(Cl_2)$ where $D(Cl_2)$, the dissociation energy of the chlorine molecule, is known.

A similar study of the phosgene reaction would yield values for $A_3 A_{Cl_2}^{\frac{1}{2}} A_{COCl}^{\frac{1}{2}}$ and $E_3 + E_{COCl} + \frac{1}{2}D(Cl_2)$ where A_{Cl_2} is the ratio of the frequency factors for the forward and back reaction:

$$M + Cl_2 \rightleftharpoons 2Cl\cdot + M$$

Bodenstein et al, in fact coupled the results from their thermal and photochemical studies of the phosgene synthesis and by estimating the values of the activation energies were able to obtain values for the individual rate constants k_3, k_5 and k_{COCl}. These values are very similar to those obtained later by Burns and Dainton, who used the accurate rotating sector method (see below), but in view of work by Benson & Buss the agreement between these separate studies seems largely fortuitous.

Benson & Buss[35] (1958) have investigated the conditions under which thermodynamic equilibrium concentrations of halogen atoms are produced. They have shown that in thermal chlorinations the stationary state for chlorine atoms is reached very slowly even at temperatures of 550°K. Unfortunately, this fact has not been generally appreciated although a large amount of thermal chlorination work has been carried out. In fact having surveyed the halogenation literature Benson & Buss concluded that almost all the chlorination systems which have been studied would have required times t_{90} in excess of 1000 sec. for the attainment of 90% stationary state concentration. Only one system was studied above 650°K at which temperature t_{90} would be 100 sec. In general a large percentage of reaction would have taken place before steady state conditions were reached, and thus the results from these studies cannot be treated by the simplifying stationary state approximation. Quantitative information from such work must therefore be treated with suspicion. However Benson does admit the possibility of heterogeneous processes being effective in allowing the stationary state to be reached more rapidly, but he maintains that this would imply the presence of a considerable amount of

concurrent wall reaction.

In conclusion it can be stated that the study of the overall rate constant from thermal or photochemical chlorinations can provide no direct information on absolute rate constants for single reactions. The simplest cases may yield approximate values of activation energies but the use of these methods alone will not allow A factor data to be obtained. More direct methods must therefore be used which essentially enable the free radical concentrations to be determined.

Let us consider a typical chain propagating reaction in an olefine chlorination

$$Cl\cdot + A = \cdot ACl \qquad (2)$$

whose rate R_2 and rate constant k_2 are defined by

$$R_2 = -\frac{d(A)}{dt} = k_2(A)(Cl\cdot)$$

In order to evaluate k_2 explicitly we have to determine (a) the concentration of olefine (b) the rate of reaction and (c) the chlorine atom concentration.

(a) The concentration of olefine can be easily obtained by keeping the percentage conversion small, whence (A) will be virtually constant throughout the reaction and can be equated to the initial concentration.

(b) Both chain propagating steps are extremely fast and if it is assumed that all ·ACl radicals produced by (2) will inevitably react by

$$\cdot ACl + Cl_2 = ACl_2 + Cl\cdot \qquad (3)$$

then $\frac{d(ACl_2)}{dt}$ can be used as a measure of R_2. $d(ACl_2)/dt$ can be easily measured either as the rate of pressure fall or as the rate of removal of chlorine (provided these quantities are known to corres-

-pond to the rate of formation of ACl_2) but a more precise and unambiguous method is to analyse for ACl_2 using gas chromatography.

(c) Of the three quantities which have to be measured, the free atom concentration is by far the most difficult, since the lifetime of the free atoms is short and their concentration is exceedingly low. For thermal systems determination of the halogen atom concentration would be most conveniently carried out by making use of the known equilibrium constant for the diatomic molecule. However, although this is the standard method for obtaining absolute rate constants for brominations, it cannot be applied to chlorination systems where the higher halogen bond strength makes the attainment of steady state conditions extremely slow. Some workers[36] have instead made use of the equilibrium constant for the reaction

$$NO + Cl_2 \rightleftharpoons NOCl + Cl\cdot$$

where the activation energies of both forward and reverse reactions are low and equilibrium is therefore rapid. Rodebush & Kingelhoeffer[9] on the other hand, in their work on $H_2 + Cl_2$ were able to use a diffusion gauge to measure directly the concentration of chlorine atoms produced by means of an electrodeless discharge.

In order to obtain rate constant data for photochemical systems it is not always necessary to measure the chlorine atom concentration directly. There are two methods which avoid this direct measurement viz;

(i) The rotating sector method in which the measurement of radical life times is employed to evaluate absolute rate constants and

(ii) 'The competitive method' by which one can obtain accurate rate constant ratios for substances chlorinated in pairs.

By using this latter method, it is possible to evaluate <u>absolute</u> rate constants for a series of substances on the basis of only one absolute rate constant measured by an independent method. This competitive

technique was the one used on this work and will be dealt with in some detail in the next section (1.4), however, for the present we will consider the rotating sector method which has been used in the study of certain chlorination systems, particularly those of the chloro-olefines.

The Rotating Sector Method:[37] The mean life time of a radical under stationary state conditions can be defined by

$$\tau_s = \frac{\text{Stationary state concentration of radicals}}{\text{Rate of removal of radicals.}}$$

For a simple reaction scheme which involves the following three main steps:

$$R_2 \xrightarrow{h\nu} 2R$$

$$R\cdot + A \xrightarrow{k_p} \text{products}$$

$$R\cdot + R\cdot \xrightarrow{k_t} R_2$$

it can be seen that

$$\tau_s = \frac{(R)_s}{k_t(R\cdot)_s^2} = \frac{1}{k_t(R)_s} \quad \ldots\ldots\ldots(a)$$

where the suffix s refers to stationary state conditions.

IF we assume the quantium yield of the initiation step is 1 (as in a chlorination reaction) then the rate of initiation = $2I_{abs}$, and under stationary state conditions

$$k_t(R)_s^2 = 2I_{abs}$$

$$\therefore \quad (R\cdot)_s = (2I_{abs}/k_t)^{\frac{1}{2}}$$

substitution of this value for $(R\cdot)_s$ in equation (a) gives

$$(2k_t)^{-\frac{1}{2}} = \tau_s I_{abs}^{\frac{1}{2}}$$

Thus knowledge of the mean radical life-time will allow the direct determination of the termination rate constant k_t. IF the complex rate constant ratio for the overall reaction is of the form k_p/k_t then a concurrent study of the overall kinetics will allow k_p to also be

evaluated.

A method for measuring radical life times experimentally is that of the rotating sector technique, which involves the study of the variation in radical concentrations under changing conditions of intermittent illumination. Intermittency is achieved by cutting the light beam by means of a rotating disc from which a segment has been removed. The sector method is only applicable to photochemical systems where the overall rate in steady light is $\propto I_{abs}^{n}$ where $n < 1$. Ideally n should be 0.5, indicating that chain termination is predominantly second order. This is the case in the above simple mechanism and we shall use this as an example.

IF the sector is made by using a disc from which a quadrant has been removed the ratio of dark to light interval produced on rotation will be 3/1. Subsequent study of the reaction using a range of sector speeds will reveal the following phenomena

At slow sector speeds where the period of rotation is much longer than the life time of the radicals, the radical concentration will have time to fall almost to zero during the dark periods and reaction can be considered to take place only during $\frac{1}{4}$ of the total time for rotation. Under these circumstances the mean radical concentration $(\overline{R})$ will $= \frac{1}{4}(R)_s$. IF on the other hand the rotational period is short compared to the radical life-times then although the radical concentration will fluctuate it will remain sufficiently high during the dark period for reaction to continue, and the overall reaction will proceed as if illuminated by light of $\frac{1}{4}$ the original intensity. Thus in this case

$$(\overline{R}) = \tfrac{1}{2}(R)_s$$

The transition in the value of the ratio $(\overline{R})/(R)_s$ from .25 to .50 takes place over a small range of intermediate sector speeds where the duration of the light flash is of the same order as the radical life time.

The radical concentration mentioned above cannot be measured directly but the measurement of the rate of some reaction first order in R· can be used instead. Such a reaction is the propagating step whose rate R_p is given by

$$R_p = k_p(R\cdot)(A)$$

Now if chains are long

$$R_p = \frac{d(A)}{dt} \text{ or } + \frac{d(\text{product})}{dt}$$

thus R_p can be easily obtained.

The ratio $(\bar{R})/(R)_s$ is then accurately given by

$$\frac{(\bar{R})}{(R)_s} = \frac{R_p \text{ in intermittent light}}{R_p \text{ in steady light of same intensity}}$$

By mathematical manipulation of the sector theory it can be shown that $(\bar{R})/(R)_s$ depends only on the mean radical lifetime τ_s, and the size and speed of the rotating sector. On this basis it is possible to draw theoretical curves of $(\bar{R})/(R)_s$ vs Log b for any sector size. The parameter b is dimensionless and = t_L/τ_s, where t_L is the duration of the light flash. IF experimentally one obtains a plot of $(\bar{R})/(R)_s$ vs Log t_L the corresponding value of τ_s can be simply evaluated by moving the experimental curve along the x axis until it coincides with its respective theoretical curve. It is apparent that the value of τ_s is simply related to the necessary displacement of the experimental curve.

Burns & Dainton[32, 38] adapted the rotating sector theory to suit the synthesis of phosgene, where the system is somewhat more complex due to the occurrence of an equilibrium and the fact that chain termination is by combination of different radical species namely Cl· and COCl. They used the rate of pressure change as a measure of the rate of reaction, and obtained experimentally the parameter

$$\rho = \frac{2 \text{ x rate with sector running}}{\text{rate in continuous light of same intensity}}$$

at various sector speeds. In this way plots of Logρ vs t_L were obtained for several reaction mixtures containing different amounts of carbon monoxide. Subsequent matching of experimental and theoretical curves gave values of τ_s.

For this system

$$\tau_s = \frac{(Cl) + (COCl}{\text{Rate of formation of radicals}}$$

and the stationary state treatment of the reaction mechanism gave

$$\tau_s = \tfrac{1}{2}\left[\frac{CO}{k_5 K_{COCl}}\right]^{\frac{1}{2}} \left[\frac{1 + K_{COCl}/CO}{I_{abs}^{\frac{1}{2}}}\right]$$

For sets of experiments where light intensity, sector speed, chlorine pressure, and temperature were kept constant whilst (CO) was varied they obtained a final equation of the form

$$\beta = \frac{C_1}{\tau_s} = \frac{K_{COCl}}{C_2 k_5}^{\frac{1}{2}} \; 1 + \frac{(CO)}{K_{COCl}}$$

where C_1 and C_2 were constants of known values. A linear plot of logβ vs (CO) allowed K_{COCl} and k_s to be obtained absolutely from the gradient and intercept. The temperature dependences gave

$$\text{Log}_{10} K_{COCl} = 2.806 - 6310/4.75T$$

and

$$\text{Log}_{10} K_5 = 11.60 - 830/4.75T$$

A combination of these values with the temperature dependence of the overall rate constant in continuous light gave an absolute value of

$$\text{Log } k_3 = 9.401 - 2960/4.75T$$

Unfortunately the sector technique suffers from several disadvantages. They are 1) The correct interpretation of the results depends on one assuming the correct form for the complex rate constant ratio for the overall reaction. (As we have seen earlier this requires a detailed knowledge of the reaction mechanism.)

2) During the time the reaction is being studied chain termination must be at least 95% second order and must be known to take place by only one type of radical combination.

3) The mode of chain termination (i.e. whether by (4), (5) or (6) dictates the chain propagating step for which information can be obtained, and usually only k_3 can be obtained (see p14).

4) The lengthy practical procedure is further encumbered by the fact that in order to obtain reproducible values for radical life times all reactants must be extremely pure.

The above requirements severely limit the extent to which the rotating sector technique can be applied to study the reaction of chlorine atoms. In fact only one determination of k_2 has been made by this method[396] and very high concentrations of chlorine were required to ensure that termination was mainly by

$$Cl^{\bullet} + Cl^{\bullet} + M = Cl_2 + M$$

1.4. THE COMPETITIVE METHOD[40]

In essence this method consists of making two substances react with a free radical source, in competition. The mode of reaction of the individual substances with the free radicals must be similar, but the nature of the free radical source is unimportant and it is not essential for stationary state conditions to be achieved.

In the work of this thesis ethylene, propylene and isobutene were competed separately with propane. In general the following chain propagating steps may be written for the chlorination of a mixture of an olefine and an alkane

$$Cl\cdot + A = \cdot ACl \qquad (2)$$

$$\cdot ACl + Cl_2 = ACl_2 + Cl\cdot \qquad (3)$$

$$RH + Cl\cdot = R\cdot + HCl \qquad (2')$$

$$R\cdot + Cl_2 = RCl_2 + Cl\cdot \qquad (3')$$

Reactions (2) and (2') will compete for chlorine atoms and the rates of the two reactions are defined as

$$R_2 = k_2(Cl)(A)$$

$$R_2' = k_2'(Cl)(RH)$$

Thus the ratio of the rate constants is given by

$$k_2'/k_2 = R_2(RH)/R_2'(A)$$

If the reaction rates can be obtained, and the known initial concentrations of RH and A are kept virtually constant by working to small percentage conversion, then the rate constant ratio can be evaluated. It should be noted that neither the chlorine atom concentration nor any term depending on the chain termination step are present in this expression. Thus the two major difficulties encountered in the determination of rate constants have been removed. Moreover if it is assumed that the chain carriers in the competing chains are similar

and will be equally affected by the presence of impurities then the necessity for rigorous purity of reactants is obviated. In actual fact the chains in the photochlorinations of both alkanes and alkenes are very similar in nature giving quantum yields of the order 10^4 - 10^6 and being strongly inhibited by oxygen. The termination step and the presence of impurities could only become important if they removed large amounts of chloroalkyl (·ACl) or hydrocarbon (R·) radicals an unlikely event provided long chains are maintained.

The competitive method has one further major advantage in that it provides data on the rate constant k_2 of the initial chain propagating step, whereas the results from other methods of investigation are usually confined to reaction (3).

It is evident that if a series of reactions are judiciously competed in pairs then independent knowledge of only one absolute rate constant will lead to the evaluation of absolute rate constants for the whole series.

The measurements of rates R_2 & R_2' may be made in two ways namely the 'consumption method' or 'the product method'.

(a) <u>The Consumption Method</u>: IF the rates are written in terms of reactant consumed, assuming that only 2 & 2' remove RH and A Then:

$$\frac{R_2'}{R_2} = \frac{-d(RH)}{dt} \Big/ \frac{-d(A)}{dt} = \frac{k_2(RH)}{k_2'(A)}$$

Therefore:

$$\frac{-d(RH)}{(RH)} \Big/ \frac{d(A)}{(A)} = \frac{k_2}{k_2'}$$

and by integration:

$$\frac{k_2}{k_2'} = \frac{Ln(RH)i - Ln(RH)f}{Ln(A)i - Ln(A)f}$$

where suffixes i and f refer to the initial and final concentrations.

Thus this method requires the measurement of concentration changes. Good accuracy can be obtained provided $k_2' \simeq k_2$ and that the consumption is around 10% of each reactant. IF however the rate constants differ markedly then the change in concentration of one reactant may be very small and difficult to measure, whilst the concentration change of the other reactant may be quite large. In this case not only will the rate constant ratio be inaccurate but the error in ΔRH will be different from that in ΔA. These errors may be lessened to some extent by changing the initial concentration ratio so that the absolute consumption of each reactant is about the same. This would however be impracticable for rate constant ratios much above 40.

(b) <u>The Product Method</u>[41]

It is reasonable to assume that if the reaction chains are long, changes in the concentrations of RH and A are almost entirely due to reactions (2) and (2'). The radicals R· and ·ACl thus formed will inevitably lead to an equivalent amount of the products RCl and ACl_2 unless significant side reactions occur. Thus these chlorides may be used as a measure of reaction progress.

$$\text{Now} \quad Ln \frac{(A)i}{(A)f} = Ln\left[1 + \frac{(A)i - (A)f}{(A)f}\right]$$

and if consumption is small

$$Ln \frac{(A)i}{(A)f} = \frac{(A)i - (A)f}{(A)f} \simeq \frac{(\Delta A)}{(A)i}$$

and similarly for $Ln\frac{(RH)i}{(RH)f}$

$$\therefore \quad \frac{k_2}{k_2'} = \frac{(\Delta RH)(A)i}{(\Delta A)(RH)i}$$

where $(A)_i$ and $(RH)_i$ are the initial concentrations.

But $(\Delta RH) = (RCl)$ and $(\Delta A) = (ACl_2)$.

Thus:

$$\frac{k_2}{k_2'} = \frac{(RCl)(A)}{(ACl_2)(RH)} \quad \text{..... .....I}$$

(RCl) and (ACl_2) can be easily and accurately determined quantitatively using gas chromatography.

For systems where $<5\%$ of each competitor are reacted equation I is satisfactory. However if the percentage reaction is greater a more precise equation is required i.e.:

$$\frac{k_2}{k_2'} = \frac{(RCl)(A)_m}{(ACl_2)(RH)_m} \quad \text{..... II}$$

where the suffix m refers to the mean concentration of reactant.

This form of the equation will give an accuracy better than 2% as long as the consumption of either reactant is $<30\%$ (see Appendix B).

Although both equations I & II have been employed in this thesis in a majority of cases the more accurate equation II was used.

In order to evaluate the mean concentration necessary for equation II detailed analytical results are required.

Thus experimentally one can obtain (ΔRH) from the following relationships

$$\frac{(\Delta RH)}{(\Delta RH) + (\Delta A)} = \frac{(RCl)_t}{(RCl)_t + (ACl_2)_t} = \frac{(\Delta RH)}{Cl_2}$$

where $(RCl)_t$ and $(ACl_2)_t$ refer to the total chloride products from alkane and olefine respectively. The mean concentration can then be calculated from

$$(RH)_m = (RH)_i - \tfrac{1}{2}(\Delta RH) \ ,$$

and similarly for (ΔA) and $(A)_m$.

In general it is advisable to use the 'mean method' as quite

apart from the increased accuracy, the calculation also provides a check on the percentage consumptions.

An extra advantage of the product method in general is that it provides an easy method for study of the relative rate constants for attack at different points in the same hydrocarbon. IF we designate the reactions at two different points as x and y then:-

$$\frac{k_x}{k_y} = \frac{(RCl)_y}{(RCl)_x}$$

The two points of attack yield distinctive chloride products which can be easily analysed by gas chromatography. IF the addition and substitution reactions of free radicals with an olefine C_nH_{2n}, proceed by similar chain mechanisms then the above method may be applied to them. Whence for chlorinations

$$\frac{k \text{ addn.}}{k \text{ subst.}} = \frac{C_nH_{2n-1}Cl}{C_nH_{2n}Cl_2}$$

where $C_nH_{2n-1}Cl$ is a chloro-olefine.

(Complications may occur in the competitive method if the initial chloride products either suffer thermal decomposition or undergo secondary chlorination. In both cases more detailed analysis will usually permit any necessary allowance to be made.)

Standard Absolute Rate Constant:- As has already been stated the competitive method will yield absolute rate constants if only one rate constant is known absolutely from an independent method.

A suitable standard absolute rate constant should be one which has been carefully obtained over a large temperature range. Accuracy is best assured if the rate constant can be reproduced by more than two independent methods of determination. Such a rate constant is that for

$$H_2 + Cl^{\cdot} \overset{2'}{=} HCl + H^{\cdot}$$

As we have already seen this system has been extensively studied but mostly by the inaccurate complex rate constant method. The present accepted value of k_2' depends on the results of three pairs of workers.

Rodebush & Klingelhoeffer[9] generated chlorine atoms, by a high frequency electrodeless discharge, and studied their reaction with Hydrogen in a flow system at 0 and 25°C. The extent of chlorine dissociation was measured directly by a Wrede-Harteck diffusion gauge. This knowledge together with the measurement of the HCl produced and the flow rate, allowed direct determination of the rate constant.

Steiner & Rideal[42] measured the thermal rate of the HCl catalysed para-to ortho-hydrogen conversion between 630° and 800°C. They thus obtained the rate constant for the reaction

$$H\cdot + HCl \overset{k_2'}{=} H_2 + Cl\cdot$$

Calculation of the equilibrium constant k_{-2}'/k_2' from thermodynamic data gave k_2'.

Ashmore & Chanmugam[36] studied the thermal chlorination of hydrogen in the presence of nitrosyl chloride at 250°C. Their scheme gave a complex rate constant ratio of the form $k_{NOCl}k_2$ where k_{NOCl} was the known equilibrium[43] constant for

$$NO + Cl_2 \rightleftharpoons NOCl + Cl$$

and again k_2 was easily obtained.

A combination of these three sets of data give a very good Arrhenius plot over a wide temperature range. Fettis & Knox[40] have recently recalculated Steiner & Rideal's value using modern thermodynamic data and a least squares treatment of the corrected Arrhenius plot gave

$$k_2 = (8.3 \pm 0.6) \times 10^{13} \exp(-5480 \pm 140/RT) \text{ cc moles}^{-1} \text{ sec}^{-1}$$

This value can be expected to have very good accuracy.

Knox & Nelson[44] using a value of k_2 very similar to the above,

competed the following series of substances in pairs. H_2 : CH_4, C_2H_6 : C_3H_8, C_2H_6 : nC_4H_{10}, C_2H_4 : iso C_4H_{10}, C_3H_8 : neo C_5H_{12}, C_2H_6 : cyclo-propane and C_3H_8 : cyclobutane.

They thus obtained absolute rate constants for chlorine atom attack on all these hydrocarbons.

For the present work propane was chosen as the standard competitor and we have made use of the absolute values of k_2 obtained by Knox & Nelson for normal and secondary, propyl chloride formation.

Applicability of the product method to propane-olefine systems:

In deriving the theory of the product method the implicit assumption was made that all the radicals formed by reactions (2) and (2') will react by (3) and (3') to yield equivalent amounts of the respective chloride products. This will not be true if any of (-2), (-2'), (-3) or (-3') proceed to an appreciable extent or if radicals R· or ·ACl are pyrolysed at the experimental temperature.

For alkanes, reactions (2') and (3') are exothermic and of low activation energy (see page 8), thus the inhibitory reactions (-3') and (-2') are endothermic and unimportant. Moreover in general and certainly in the case of propane[45], more than 30 k. cals. activation energy are required for pyrolysis of R· radicals, and loss of R· by this means is only significant above 300°C.

For alkenes information on chlorinations is less complete. However (2) and (3) are still exothermic and of near zero activation energy, but (-2) is now unimolecular and therefore around 10^5 times faster than a corresponding alkane reaction with the same activation energy*. Goldfinger[46] has shown that D(A -Cl) decreases with increasing

*(This applies at a pressure of about 1/5 atmosphere at N.T.P.)

chloro-substitution of the parent olefine and for the most chlorinated simple olefine C_2Cl_4 he obtained

$$D(C_{Cl_4} - Cl) = 16.8 \text{ k. cal.}$$

As the experimental activation energy for:-

$$C_2Cl_4 + Cl\cdot = C_2Cl_5\cdot \qquad (2)$$

was 0 k. cal., E_{-2} must be $\sim$17 k. cal. and thus reaction (-2) which competes with (3) for the $\cdot ACl$ radicals will become important at about 150°C. (For C_2Cl_4, $Log_{10}k_3 = 8.31 - 1186/T$). The change in mechanism accompanying the onset of this decomposition has in fact been observed.

Assuming $D(C_2H_5 - H) = 96$ k. cal. Goldfinger used a thermochemical cycle to obtain an estimate for $D(C_2H_4 - Cl)$ of $\sim$24 k. cal. He also obtained a value of 80 k. cal. for $D(C_2H_4Cl - Cl)$.

IF we assume E_3 for ethylene = E_3 for vinyl chloride $\simeq$1 k. cal.[48] E_{-3} can be calculated from Goldfinger's * data to be around 21 k. cal.

By taking the values of $Log_{10}k_2$ and $Log_{10}k_3$ for ethylene as being near those obtained for vinyl chloride[49] viz. 10.3 - 1500/4.57T and 8.75 - 920/4.57T respectively[48], it can be readily seen that neither reaction (-2) which competes with (3), nor (-3) which competes with (2), is likely to be significant below 150°C even for chlorine concentrations as low as 0.08 mM/litre (i.e. 1.5 mm at 300°K).

On the basis of the above it appears that the propane-ethylene system should be capable of successful study up to 150°C using the product method.

In considering propene and isobutene it may be noted that the initial addition of a free radical to an olefine of general form $RCH = CH_2$

* In reference 46 Goldfinger has collected a table of the other relevant thermodynamic data. The heats of formation of C_2H_4, $C_2H_4Cl_2$ and $\cdot Cl$, in their standard states at 298°K are given as + 12.5, - 31.4 and + 28.94 respectively.

takes place on the carbon atom of the $-CH_2$ group.[50] Moreover the stability of the radical so formed increases in the sequence

$$(-\dot{C}H_2) < (\geq CH\cdot) < (\geqslant C\cdot)$$

Thus the tertiary

$$CH_3 - \dot{C}(CH_3) - CH_2Cl$$

radical produced from isobutene would be expected to be more stable than the secondary $CH_3 - \dot{C}H - CH_2Cl$ radical produced from propene which again should be more stable than the primary $\cdot CH_2 - CH_2Cl$ radical from ethylene. This may be interpreted as meaning that D(A -Cl) increases from ethylene to isobutene and thus the temperature at which reaction (-2) becomes important should increase accordingly.

The strong tendency for a radical of the type $-\dot{C}H-CHCl-$ to lose HCl and form an olefine, has been reported[51]. This phenomenon known as the 'vicinal effect' will occur in the case of the chlorination of propene but does not become important till about 200°C. The chloro tertiary butyl radical obviously cannot undergo elimination of HCl in this way, though it does appear that there may be some steric hindrance to subsequent formation of the 1.2 product.

It seems then that it should also be possible to study both propene and isobutene systems successfully.

Competitive Chlorinations

Although many competitive chlorinations have been carried out, little reliable data were obtained until the introduction of gas chromatographic methods of analysis which allowed the accurate 'product method' to be easily applied.

Some of the earliest competitive work with chlorine atoms was on H_2 and HD mixtures in 1934[52], whilst Hass et al.[53] using a flow system were the first to competitively chlorinate mixtures of hydrocarbons and

also study the relative rates of reaction at different positions in the same molecule. They used a crude distillation method to separate the products and their results do not agree with later work.

Pritchard, Pyke and Trotman Dickenson[54] studied further hydrocarbon mixtures using the 'consumption method'. Difficulty was encountered in systems such as H_2 : CH_4 and CH_4 : C_2H_6 where the reactivities of the competitors differed greatly.

Knox[41] was first to apply chromatography to competitive experiments and his work has been extended by Anson, Fredericks[55] and Tedder, Knox & Nelson[44] and Fredericks & Tedder[56]. The systems studied by Knox & Nelson have already been mentioned.

Comparison of the results from the three sets of workers, where they studied the same hydrocarbons, show good agreement.

By combining results of Knox[57] on the competitive chlorination of the chloromethanes versus methane and propane, and the results of Knox & Nelson, two circuits of competitive chlorinations can be set up as follows;

(1) Methane, ethane, propane, methylene chloride, methane

(2) " " " methyl chloride, chloroform, methane.

Every adjacent pair have been competed and the agreement within the two circuits emphasises the reliability of the Arrhenius parameters obtained by competitive methods[57].

Goldfinger[47] et al. have competed tetrachloroethylene with pentachloroethane, and also with the chloromethanes, between 360° and 475°K. A combination of their results with Knox's absolute parameters for the chloromethanes, gave E_2 for C_2Cl_4 = 0 and E_2 for C_2HCl_5 = 3.4. k.cal. The value of zero suggests that the absolute scale based on the hydrogen-chlorine reaction is correct.

1.5. HALOGENATION OF OLEFINES (Especially Chlorination)

The bulk of the work published on halogination of olefines has been of a qualitative nature, and concerned with reactions in solutions. This work does not concern us here directly, but mention will be made of certain papers where it is felt this helps to complete the overall picture. Values of reliable Arrhenius parameters will not normally be quoted in the text but a table is given at the end.

Ethylene:

All the early work on ethylene halogenation was complicated by a variety of surface effects. Around 1923 several investigations were made on the bromination and chlorination reactions with a view to deciding the mechanism of addition to double bonds. Stewart and Edlund[58] reacted ethylene and bromine at 0°C. The reactants, which were carried on separate streams of air, passed into a baffled mixing tube before entering the thermostated reaction vessel. The inlet to the RV was then closed and whilst the system was illuminated by a 100 Watt Tungsten lamp, the reaction rate was obtained from the fall in pressure. Using a constant dry RV surface they found the reaction was second order and its rate was $\propto (C_2H_4)(Br_2)$. The specific reaction rate during the first 12 seconds of reaction was apparently greater than the subsequent rate, and this was thought to be due to wall catalysis. They expected to observe a 10 mm pressure increase due to the heat of reaction but as none was observed an entirely heterogeneous reaction was assumed to take place. In fact the condition of the glass surface appeared to be important as addition of water vapour increased the rate and made the results irreproducible.

Norrish[59] suggested that the polar nature of water accounted for its catalytic activity; the polarity being sufficient to distort

the adjacent reactant molecules and make them more susceptible to reaction. In order to test this hypothesis he studied the above reaction in vessels coated with, stearic acid, cetyl alcohol and paraffin wax. The polar stearic acid was found to increase the rate by a factor of 1.5 over the rate on clean glass, whilst cetyl alcohol reduced the rate and the non polar paraffin wax almost inhibited reaction. A further similar study on the chlorination[60] of ethylene in the dark produced very much the same results, although the paraffin wax coating was found to be seventy times more deactivating than for the bromine reaction. Addition of water vapour had no effect on the paraffin wax system, whilst a 30% increase in rate was observed in the corresponding case for a clean glass surface. IF this activation is explained in terms of modification of the surface by adsorbed water then the above observation is not unreasonable as the non polar paraffin wax would not be expected to adsorb water to any extent.

It should be noted at this point that the large concentrations of oxygen present in the above systems would effectively inhibit any free radical reactions thus there can be no question of impurities introduced in the drying process being the cause of the observed decrease in rate on desiccation; unless of course molecular halogen was removed.

Stewart & Smith[61] studied the chlorination of ethylene in a pyrex vacuum system at room temperature, with and without the presence of oxygen. The RV was prepared before each reaction by baking it at 550°C and light was rigorously excluded. They found that the short induction period which occurred under these conditions was unaffected by HCl but was almost completely removed by addition of $C_2H_4Cl_2$ or $C_2H_3Cl_3$ to the initial reaction mixture. The catalytic effect of these latter two compounds was much less in the presence of oxygen.

In the absence of oxygen they observed both addition and substitution reactions, the products being mainly $C_2H_4Cl_2$ and $C_2H_3Cl_3$ respectively. The amount of substitution was determined by titration of the HCl produced. As they claimed $C_2H_4Cl_2$ did not normally chlorinate under these conditions, they referred to the substitution as being 'induced' by the addition reaction. This led them to postulate[62] the initial production of an activated ethylene dichloride molecule $C_2H_4Cl_2^*$ as follows:-

$$C_2H_4 + Cl_2 \xrightarrow[\text{catalyst}]{} C_2H_4Cl_2^* \text{ (on the surface)}$$

which reacted by

$$C_2H_4Cl_2^* + Cl_2 = C_2H_3Cl_3 + HCl + \text{heat}$$

$$C_2H_4Cl_2^* \xrightarrow[\text{deactivator}]{} C_2H_4Cl_2$$

As the substitution reaction was almost completely inhibited by oxygen they assumed oxygen acted as a particularly efficient deactivator (see later page 37).

They believed that perfectly dry ethylene-chlorine[63] mixtures would not react in the dark and therefore assumed gas phase reactions could not be taking place. The entirely heterogeneous reactions were therefore supposed to be catalysed by the glass surface and/or the presence of surface films of $C_2H_4Cl_2$ or $C_2H_3Cl_3$. Autocatalysis was also observed and this was attributed to the products being more efficient catalysts than the clean glass surface.

Stewart & Hanson[64] managed to 'induce' the chlorination of benzene in the dark at room temperature by bubbling ethylene into a solution of chlorine in benzene. They obtained both addition and substitution products from benzene and from ethylene (substitution gave $C_2H_3Cl_3$), and suggested radical chain mechanisms for all reactions. It

seems likely however that ionic processes were also present. Ionic mechanisms have been suggested by Taft[65] and more recently by Kuriacose et al. for reactions of chlorine with ethylene, isobutene and higher olefines, in the liquid phase. Kuriacose[66, 67] et al. used solutions in cyclohexane or carbon tetrachloride, in the dark and at room temperature.

Two further points may be raised on the papers mentioned so far.

(i) In the chlorination of ethylene in the dark Stewart & Smiths' observation that the substitution reaction fofming $C_2H_3Cl_3$ was inhibited by oxygen must surely mean that this process unlike the addition reaction was purely free radical in nature. Chlorination of $C_2H_4Cl_2$ alone in the dark would not therefore be expected to occur at room temperature, and in fact it was claimed that no reaction took place under these conditions. It seems then that the so called 'induced' formation of $C_2H_3Cl_3$ which they observed when ethylene was chlorinated in the dark occurred through the agency of chlorine atoms produced in some way as a result of the addition reaction.

(ii) The presence of liquids or the formation of liquid products will both give apparent 'enhanced' rates using the method of pressure fall. The extent of this enhancement will be somewhat difficult to estimate as not only will (a) products condense as soon as they are formed (which would double the observed pressure drop) but also (b) solution of reactants may take place. Whilst Stewart et al. were aware of point (a) it is not clear whether they made any allowance for it in the interpretation of their observed rates. However if we accept their catalyses as being real (some of the work in this thesis supports their findings) then, if sufficient liquid is present one cannot rule out the possibility of ionic reactions taking place in the liquid phase.

Stewart & Wiedenbaum[68] investigated the photo-chlorination of

ethylene in the absence of oxygen at 27°C. Before each run the R.V. was 'cleaned up' by exploding a mixture of hydrogen and chlorine in it and then evacuating to 10^{-5} - 10^{-6} mm Hg. They obtained the rate expression

$$-d(Cl_2)/dt = KI_{abs}$$

and proposed a chain mechanism concluding that ethylene must have a very high collision efficiency in order that over wide limits its concentration should not effect the rate. However the work reported in their paper does not prove this statement as no concentration range was quoted. When they reacted a mixture of hydrogen and ethylene in the dark the hydrogen did not react. Even when a mixture containing 9.64 times as much hydrogen as ethylene was photolysed only 10.7% of the chlorine reacted with the hydrogen. This data gives a rate constant ratio

$$\frac{k_{H_2}}{k_{C_2H_4}} = \frac{1}{80.7}$$

We know k_2' for H_2 (p29) and if we take A_2 for ethylene to be the same as that obtained for vinyl chloride[11] i.e. $A_2 = 10^{10} \times 2$ litre moles^{-1} sec^{-1}, then E_2 for ethylene = 2.0 k.cals. This value is reasonably in line with that estimated recently for vinyl chloride viz 1.5 ± 1 k.cal.[57]

Vaughan and Rust[69] chlorinated ethylene thermally using a flow system with Nitrogen or carbon dioxide as carrier gas. The addition reaction was very slight below 220°C, whilst substitution only began at higher temperatures but became progressively more important being finally the main reaction above 400°C and yielding both vinyl chloride and $C_2H_3Cl_3$. Traces of oxygen up to 0.5% were found to catalyse the substitution reaction whilst larger amounts of oxygen inhibited reaction completely below 285°C. This inhibition became less effective with rise in

temperature or increase in surface/volume ratio.

The rate of reaction was roughly

$$\propto (Cl_2)(C_2H_4)^{\frac{1}{2}}$$

but results were poorly reproducible due to surface effects. Ethylene was found to have a reactivity intermediate between ethane and ethyl chloride, ethane reacting the more rapidly. The reaction could be promoted below 210°C by the use of lead tetraethyl and they proposed free radical chains for both the addition and substitution reactions in the absence of oxygen. These mechanisms did not however yield the experimental rate law.

A careful study of the photochemical bromination and also chlorination of ethylene was undertaken by Schmitz[70] et al. in a quartz vessel using light of 4358A wavelength. For both reactions the quantum yield was of the order 10^5 - 10^6 and homogeneity was claimed. From the brominations between 60° & 80°C they found the rate strongly dependent on total pressure, ethylene itself having a much greater effect than other gases. The rate expression changed from low to high pressures consistent with a change from heterogeneous to homogeneous chain termination; by bromine atom recombination. They estimated E_2 as ~0 k.cal.

For chlorinations, reactions were carried out between 25° and 40°C only, because Schmitz et al. claimed the 'thermal' reaction was far too rapid above these temperatures! At pressures above 10 cm they obtained the rate expression

$$R_{C_2H_4Cl_2} = k(I_{abs})^{\frac{1}{2}}(Cl_2)(C_2H_4)^{\frac{1}{2}}$$

and explained this in terms of a system analogous to that of phosgene, (p11) with the presence of the thermal equilibrium

$$\cdot Cl + C_2H_4 \underset{k-2}{\overset{k_2}{\rightleftharpoons}} \cdot C_2H_4Cl$$

Thus $K = k_3/k_5^{\frac{1}{2}}K_{C_2H_4Cl}^{\frac{1}{2}}$

The equilibrium was supposed to be achieved, reaction (3) being slow relative to (-2). However we have seen there is ample evidence (p) for us to doubt the validity of this statement at this low temperature. These workers obtained only a small temperature coefficient, and by analogy with the $COCl_2$ reaction estimated, $E_2 \sim 0$, $E_2 \sim 8$, $E_3 \sim 7$, and $E_5 \sim 1$ k. cal. Inhibition by oxygen without a sensitised oxidation was attributed to preferential reaction of the C_2H_4Cl radical with oxygen.

In the period 1961-62 Dainton and co-workers published a series of papers on the photochlorination of the chloro-ethylenes, using the rotating sector techniques. The mechanisms worked out for these reactions were all very similar and will be dealt with in some detail later but at this stage it is only necessary to note that they found the corresponding ethylene[48] system too complex to study by the rotating sector method, their chlorine dependence being of the form

$$Cl_2 / \left[a + b(Cl_2) \right]^{\frac{1}{2}}$$

The most recent work published on ethylene was in 1962 by Chaikin[71]. He used the method of differential calorimetry to determine the degree of heterogeneity in the thermal chlorination <u>in the dark</u>. This method consists in principle of measuring the difference in temperature between the axis of the reaction vessel and the walls, during a reaction, and comparing the measured value with that calculated assuming an entirely homogeneous reaction. The ratio

$$\rho = \Delta T \text{ Experimental} / \Delta T \text{ Homogeneous}$$

is a measure of the homogeneity and obviously = 1 for an entirely homogeneous reaction.

Chaikin measured ΔT Expt. by using four thermocouples in series and claimed an accuracy of $\pm$ ·001°C. All parts of the system

exposed to chlorine and ethylene were carefully protected by light-proof paper. Temperatures between 150° and 250°C and pressures from 5 - 20 cm were used and having shown by analysis for HCl that substitution did not exceed 5% under these conditions he took the pressure change as a measure of the rate of the reaction

$$Cl_2 + C_2H_4 = C_2H_4Cl_2$$

He found that 30% of oxygen reduced the rate by a factor of 200 and the calorimetric measurements indicated that as the oxygen concentration increased, ρ decreased to a value near that calculated for an entirely heterogeneous reaction. Furthermore increasing the S/V ratio in systems where oxygen was present, increased the rate of reaction whereas the oxygen free system was unaffected by a change in S/V! These results were interpreted in terms of a gas phase chain reaction which was progressively replaced by a surface reaction as the oxygen concentration increased.

In theory this differential calorimetric method should be able to provide very good information about hetero-homogeneous systems. Certain facts however make precise interpretations difficult. The calculated temperature differences for a homogeneous reaction are given by the equation

$$\Delta T \text{ hom} = K\ Q\ R/\lambda$$

where K is a proportionality factor, R the reaction volocity, λ the thermal conductivity of the reaction mixture and Q the heat of reaction. Q can be calculated in most cases from adequate thermodynamic data but the heat capacity data required to determine λ is limited and usually only rough approximations can be made.

In the paper under discussion several features make acceptance of the results 'in toto' inadvisable.

Firstly the 'entirely homogeneous' reaction gave a ρ of 0.7 instead of 1 as the theory predicts. Secondly he found he could get temperature rises dissimilar by a factor of two at different distances down the themocouple capillaries. Both these points show that he did not allow for, or minimise, heat loss along the thermocouples and capillary sheaths (It might be argued that the fact ρ never equalled one implied that the reaction was never entirely homogeneous. Whilst one might suspect this to be true it would contradict his finding that change in S/V for the oxygen free system had no effect).

Finally he obtained activation energies from the temperature dependence of the rate, of 19 k. cal. for the overall homogeneous dark reaction and 35 k. cal. for the reaction in oxygen. Dainton[48] obtained E_o = 0.78 k. cal. for the overall photochemical reaction with vinyl chloride thus it is extremely unlikely that Chaikin's value is for a free radical chain reaction, as suggested.

It can be seen then that the work done on ethylene halogenations is legion and to some extent contradictory. There can be no doubt that surface effects are present but one particular obscurity is why the presence of oxygen should cause an apparently inert mixture of ethylene and chlorine at room temperature to react rapidly on the wall in the dark. In fact the work presented here shows this not to be true as dark reaction does occur at room temperature, in complete absence of oxygen.

Propene and Higher Olefines

Very little detailed photochemical work has been done on these systems.

Rust & Vaughan[72] investigated the high temperature thermal chlorinations of propene, 2-butene and isobutene in a flow system. In general the observations were similar to those for ethylene. At temperatures below 240° increase in surface area increased the reaction rate, glass wool being particularly effective in this respect. An oxygen catalysed substitution occurred with propene at low oxygen pressures but all systems were completely inhibited by larger quantities of oxygen. The amount of oxygen necessary for complete inhibition increased in the order

$$C_2H_4 < C_3H_6 < iC_4H_8$$

Percentage substitution increased in a like manner and became more important with increasing temperature. The isobutene reaction became violent above 240°C.

Groll & Hearne[73] found that for propene below 200°C addition predominated whilst at 600°C, 78% of reaction formed allyl chloride. They studied certain other olefines and determined the temperatures at which substitution began to predominate. They found the temperatures fell from ethylene to isobutene thus C_2H_4 250-350°, C_3H_6 200-250°, 2 Butene 150-225°C, 2 Pentene 125-200°C, isobutene below 40°C. In fact it appeared that for isobutene addition might never exceed substitution. Our work confirms that substitution predominates for isobutene at 35°C at least for pressures above 1 cm.

Work on chlorination of liquid isobutene has been carried out[74] in the dark and gave 87% Methallyl chloride, 3% $\beta\beta$ dimethyl vinyl chloride, 1% tertiary butyl chloride and 9% 1.2 addition; whereas HCl did not add to isobutene in the vapor phase it combined readily in the liquid phase.

Gas phase chlorination in a flow system at 0°C gave very rapid reactions. For flows of 240 cc/min of Cl_2 and 360 cc/min of isobutene the estimated reaction times were less than the apparent contact time and were claimed to be ~·006 sec. In the presence of light the amount of addition was increased but if any liquid phase formed the resulting liquid phase reaction was much more rapid than the photolytic process.

Flows of dried chlorine and isobutene apparently did not react in the dark at 150°C, but on reduction of the temperature to 65-70° liquid phase formed and all the chlorine was consumed. This seems dubious as the boiling points of Cl_2 and isobutene are -35° and -6.6°C respectively, thus any liquid phase must have been due to previous dark reaction. The major product reported above in similar investigations at lower temperatures was methallyl chloride which has a boiling point of 71-74°C and visible condensation of this substance on the walls at 65-70° with a subsequent rapid liquid phase reaction seems the most likely explanation.

Mayeur, Kuriacose[67] et al. studied the chlorinations of ethylene, octene-1, isobutene, butene-2, hexene-1, methallyl chloride and cyclohexene in carbon tetrachloride or cyclohexane solution and with or without radical inhibition. They came to the conclusion that straight chain olefines gave almost only addition products whilst those with substitution on the carbon atom of the double bond gave almost only substitution. This concurs with Taft's ionic theory[65] for these reactions, reactions taking place preferentially at points of high electron density. However these workers also claim the presence of radical reactions which set-in after an induction period.

1.6. PHOTOCHLORINATION OF CHLORINATED OLEFINES

The bulk of the work on chloro-olefines has been carried out in recent years by the schools of Dainton at Leeds and Goldfinger in Brussels. Schumacher and his school carried out extensive preliminary investigations around 1937, using the less informative overall rate constant method employing pressure measurements to determine the rate. In almost all cases Schumacher studied the corresponding bromine reactions but these will not be considered here.

Isomerization of cis & Trans 1.2. Dichloro ethylene during photochlorination[75]

This isomerization provided the key for the interpretation of chloro-olefine systems by Dainton et al. Previous work on the photochlorination of tetrachloroethylene[76] and trichloroethylene[77] had shown that the kinetics were explicable in terms of the scheme given in Appendix A, when (-2) and (-3) were neglected.

For both these systems the rate was independent of (A) above a certain characteristic concentration and was given by

$$R_p = \frac{d(ACl_2)}{dt} = k_3(Cl_2)(2I_{abs}/k_4)^{\frac{1}{2}}$$

Ayscough[75] et al. estimated the life time of an ACl radical in a normal photochlorination system as being about 10^{-5} sec, after which it would react with chlorine by reaction (3). However in principal reaction (-2) could occur, and in the case of the 1.2 dichloroethylene systems if k_{-2} approached $k_3(Cl_2)$ in value, the life time of the 1.1.2 trichloroethyl radical would be sufficient for many free rotations around the C-C bond with the result that isomerization would occur.

Concurrent photochlorination would lead to the rate expressions

$$R_i/R_p = x\, k_{-2}/k_3(Cl_2) \quad \text{for pure cis}$$

and $$R_i/R_p = (1-x)\, k_{-2}/k_3(Cl_2) \quad \text{for pure trans.}$$

Where R_i = rate of isomerization, and x and 1-x are the probabilities of forming the cis and trans isomers respectively.

Now thermal dehydrochlorination studies had suggested[78]

$$E_{-2} = 22 \text{ k. cal for } C_2H_3Cl_2$$

and $$A_{-2} = 10^{13} \text{ sec}^{-1}$$

whilst the corresponding values for reaction (3) were

$$E_3 = 2.7 \text{ k. cal}$$

and $$A_3 = 10^{8.7}$$

thus reaction (-2) would not be expected to be significant below ~200°C. However they observed appreciable isomerization at 30°C even in the presence of 200 mm of chlorine. A detailed investigation was therefore carried out. Photolyses were done in a cylindrical quartz vessel, using 200 mm of chlorine and following the reaction up to ~8% consumption of chlorine after which the excess chlorine had to be distilled-off. However they could not obtain reproducible results, even when distillation was carried out in complete darkness. Only the inhibition of further reaction by addition of nitrosyl chloride to the products engendered reproducibility. Thus some liquid phase reaction must be possible in the dark.

The relative rates R_i/R_p were obtained for systems initially containing pure cis, and also for systems containing pure trans 1,2 dichloroethylene. For both

$$R_i/R_p = \left[\text{yield of isomeric } (CHCl_2)_2\right] / \left[\text{yield of } C_2H_4Cl_2\right]$$

Product analysis was by gas chromatography.

For pressures of isomer between 30 and 80 mm using 100 mm of

chlorine, R_i/R_p varied unsystematically by $\pm$ 10% and was therefore taken to be independent of olefine pressure. On the other hand a linear dependence on $(Cl_2)^{-1}$ was observed for systems containing 40 mm of isomer, giving a positive value of R_i/R_p when $(Cl_2)^{-1} = 0$.

The values of R_i/R_p were very much larger than expected from the approximate Arrhenius parameters for reaction (-2), neither did they vary with temperature in the anticipated manner. Furthermore the $(Cl)_2^{-1}$ dependencies should have gone through the origin. Several explanations were tested but only one was meaningful.

They proposed that 2 be replaced by

$$\begin{matrix}\text{Cis} \\ \text{or} \\ \text{Trans}\end{matrix} \quad A + Cl \underset{2_t}{\overset{2_c}{=}} ACl^*$$

where ACl^* is a $C_2H_2Cl_3$ radical which contains vibrational energy greater than that for the ground state by an amount = $E_2 + \Delta H_2$. As $E_2 \simeq 0$ this energy amounts to that of $D(C_2H_2Cl_2 - Cl)$ i.e. $\simeq$ 22 k. cal. Since this is the energy equivalent to the transition state for (2) it is also that for the transition state of (-2) and therefore (-2) can occur without the need for further activation. In fact ACl^* can have a variety of fates designated α, β, γ, and δ viz.

$$\overset{\alpha}{=} \quad x \text{ Trans } A + (1-x) \text{ cis } A + Cl$$

$$+Cl_2 \quad \overset{\beta}{=} \quad y \text{ Trans } A + (1-y) \text{ cis } A + Cl_3$$

$$+Cl_2 \quad \overset{\gamma}{=} \quad ACl + Cl_2^* \quad \text{(deactivation)}$$

$$+A \quad \overset{\delta}{=} \quad A + ClA^* \quad (\cdot Cl \text{ atom exchange})$$

Where β is a chlorine atom abstraction reaction and is alternative to (3).

The isomerization rates are now given by

$$\text{for pure cis} \quad R_i/R_p = yk\beta/k + xk\alpha/k\gamma(Cl_2)$$

$$\text{and for pure Trans} \quad R_i/R_p = (1-y)\, k\beta/k\gamma + (1-x)\, k\alpha/k\gamma(Cl_2)$$

Values of x, y, $k\alpha/k\beta$, and $k\gamma/k\beta$, were calculated from the experimental data. The intercepts obtained at $(Cl_2)^{-1} = 0$ were thus accounted for.

As ACl * already contains transition state energy one would not expect x, y, or $k\alpha/k\beta$ to be dependent on temperature. In concordance the calculated values do not show any trends. $(k\beta + k\gamma)$ can be considered to = Z i.e. the collision rate of Cl_2 with ACl. * Z is approximately 10^{11} sec^{-1}, which makes $k \sim 10^8$ sec^{-1}. The life-time of the ACl * radical before spontaneous decomposition will therefore be about 10^{-8} sec. This is 10^{-3} sec shorter than the life time originally proposed for the unactivated $\cdot$ACl but should still be sufficient to allow internal rotation before destruction.

The isomerization produced by reaction was not discussed in the original publication but if significant a dependence of R_i/R_p on olefine pressure would be evident. The absence of such a dependence has not as yet been adequately confirmed[79].

Photochlorination of Cis & Trans dichloroethylene

Muller & Schumacher obtained

$$R_p = k_3 I_{abs}^{\frac{1}{2}} (Cl_2)/k_4^{\frac{1}{2}}$$ [80, 81, 82]

and $E_3 - \frac{1}{2}E_4 = 3 \cdot 1 \rightarrow 3 \cdot 5$ k. cal

for both systems.

Ayscough et al.[39] used the reaction scheme already given and studied the photochlorination of cis dichloroethylene. On the basis of this scheme at high pressures of A when all chlorine atoms will react by ^2c, the rate is given by

$$R_p = 2^{\frac{1}{2}} k_3 (Cl_2) I_{abs}^{\frac{1}{2}}/k_4^{\frac{1}{2}}$$

(which is very similar to Muller's expression). This was shown to be correct for pressures of A of 30 mm or more. The overall Arrhenius

parameters were found using four measurements of R_p between 30 & 65°C. Pressure changes were followed up to 20% reaction and were measured in a volume of 49cc whilst the illuminated volume was only ~20cc this would have been expected to produce significant errors if the dark reaction had not been relatively small. (They reported the dark reaction as 0.2% of the photo-rate).

The overall parameters were

$$E_o = 2.49 \text{k.cal} = E_3 - \tfrac{1}{2}E_4$$

$$\text{and } \text{Log}_{10}A = 3.58$$

Subsequent sector measurements of the mean lifetime of the $\cdot C_2H_2Cl_3$ radical gave k_4 and thus k_3 was calculated from k_o.

The general reaction scheme at low pressures of A, in absence of wall termination, when 2_c is rate determining gives-

$$R_p = \frac{\left[2I_{abs}/k_6(M)\right]^{\frac{1}{2}} k_{2c}(A)k\gamma(Cl_2)}{k\alpha + (k\beta + k\gamma)(Cl_2)}$$

which reduces at high chlorine concentration to

$$R_p = \frac{\left[2I_{abs}/k_6(M)\right]^{\frac{1}{2}} k_{2c}(A)k\gamma}{(k\beta + k\gamma)}$$

These investigators found that for pressures of A below 5mm R_p was approximately proportional to (A) as predicted. However although the dependence on chlorine concentration decreased with increasing chlorine pressure, a mixture of 2.1mm of A and 300mm of chlorine, gave an exponent of 0.85 for the light intensity I_a. They interpreted this as representing 70% linear termination on the walls but were unable to reduce this value below 50% by changing cell dimensions and light beam diameter, even in the presence of 280mm of carbon dioxide. Nevertheless they devised a method by which to determine the kinetic lifetime for both linear and

mutual termination, from sector measurements. The average value τ, of these life-times, was then used to obtain the stationary concentration of chlorine atoms ($= 2I_{abs}\tau$).

$$\text{Now } k_{2C} = \frac{R_p(1 + k_\beta/k_\gamma)}{(Cl)(A)}$$

thus they obtained k_{2C} at 39° and 62°C.

Trichloroethylene Photochlorination

Muller et al.[83] obtained an entirely analogous equation to their previous one for dichloroethylene, and $E_3 - \frac{1}{2}E_4$ was found to be ~5.4 k. cal. Trichloroethylene was found to undergo a chlorine sensitized oxidation.

Dainton undertook two separate investigations of this system.

The first confirmed[84] the rate equation as

$$R_p = k_o I_{abs}^{\frac{1}{2}}(Cl_2)$$

for pressures of A above 15 mm and a temperature of 140°C. As before the Arrhenius parameters were evaluated for k_3 and k_4 using a combination of rotating sector work and k_o determination. The dark rate was only 0.1% of the true photo rate but as a precaution all runs were done in a darkened room. R_p was proportional to (A) below 8 mm pressure of olefine. Their values gave

$$E_3 - \tfrac{1}{2}E_4 = 4.9 \text{ k. cal}$$

with which Muller's less accurate value agrees.

In the second investigation[49] the trichloroethylene was competed against cis 1.2 Dichloroethylene and the activated free radical scheme was applied to both. This gave by the usual competitive rules

$$\frac{R}{R^x} = \frac{k_2(A)\left[1 + \{k^x_\alpha + k^x_\beta\ (Cl_2)\}/k^x_\gamma\ (Cl_2)\right]}{k_2^x\ (A^x)\left[1 + \{k_\alpha + k_\beta\ (Cl_2)\}/k_\gamma\ (Cl_2)\right]} \quad \ldots\ldots\ldots X$$

where R^x is the rate of formation of pentachloroethane.

Rearrangement of equation X gave

$$\frac{R(A^{x})}{R^{x}(A)}\left[1+\frac{k\alpha + k\beta(Cl_2)}{k\gamma(Cl_2)}\right] = \frac{k_2}{k_2^{x}}\left[1+\frac{k^{x}\beta}{k^{x}\gamma}+\frac{k^{x}\alpha}{k^{x}\gamma\,(Cl_2)}\right] \ldots\ldots \text{Y}$$

The rate ratio was obtained from the ratio of the respective products; the photochlorinations being allowed to proceed to 8% reaction. The fact that the L.H.S. of equation Y was found to be independent of the olefine ratio and the temperature, but gave a linear dependence on $(Cl_2)^{-1}$ with a positive intercept at $(Cl_2) = 0$ was taken as a good indication that the activated intermediate mechanism did in fact apply to both reactions. The values of the ratios $k_\alpha : k_\beta : k_\gamma$ were known or interpolated from previous work (see above) but as k_α can only be measured directly for the 1.2 dichloroethylenes this competition did not allow the determination of k_2/k_2 explicitly. However on the basis of the very slight temperature dependences of the terms in large brackets in equation Y they came to the conclusion k_2/k_2 must be virtually independent of temperature. Thus E_2 for C_2HCl_3 was taken to be almost identical to that already found for cis 1.2 $C_2H_2Cl_2$, the confidence limits being adjusted according to the slight temperature dependence.

(It may be noted that in the publication of the C_2HCl_3 work a graph showing a negative dependence of the L.H. side of equation X on $(Cl_2)^{-1}$ was exhibited. The theory predicts a positive gradient, however, in view of the fact that the corresponding graphs for vinyl chloride system showed the desired dependence, it has been assumed here, that an inadvertent inversion of the ordinate has occurred. Confirmation of this from the original data has not yet been possible.)

Huybrechts et al.[86] extended the investigation of the trichloroethylene photochlorination up to 500°K. They found that above 410°K the reaction rate could no longer be obtained from pressure

measurements as a pressure minimum was observed which was followed by a pressure maximum and then a second pressure minimum. Mass spectrometry was used to elucidate the reaction in this region and it was found that the following additional reactions fitted the observations.

$$C_2HCl_5 + Cl\cdot = C_2Cl_5^{\cdot} + HCl \qquad (2')$$

$$C_2Cl_5^{\cdot} + Cl_2 = C_2Cl_6 + Cl\cdot \qquad (C)$$

$$\cdot C_2Cl_5 = C_2Cl_4 + Cl\cdot \qquad (d)$$

$$C_2Cl_4 + Cl\cdot = \cdot C_2Cl_5 \qquad (-d)$$

The reactions (C), (d), (-d) correspond to (3), (-2) and (2) in the chlorination system of C_2Cl_4.

Using the rate equation derived from the more complete reaction scheme they were able to follow $k_3/k_4^{\frac{1}{2}}$ up to 500°K and obtained a value for the temperature dependence of $Log_{10}k_3/k_4^{\frac{1}{2}}$ in very good agreement with that obtained by Dainton.

The temperature dependences of several complex rate constant ratios were obtained by suitable stationary state treatments of the complete reaction scheme and a combination of these with Dainton's value for Log k_4 for C_2HCl_3 and Goldfinger's value for Log k_2' for pentachloro-ethane[23], allowed the evaluation of the equilibrium constant for

$$\cdot C_2HCl_4 \rightleftharpoons C_2HCl_3 + \cdot Cl$$

They obtained

$$\text{Log } k_{-2} - \text{Log } k_2 = 3.97 - 20400/4.57T$$

which gave

$$D(C_2HCl_3 - Cl) = 20.4 \text{ k. cal.}$$

Their reaction scheme did not include Dainton's activated intermediate and this observed dissociation energy, which is clearly that of a normal

C_2HCl_4 radical, was taken as good indication that any activated free radicals formed were rapidly thermalized under these conditions.

They also obtained

$$\text{Log } k_5 = 10.85 \pm 1$$

where (5) is the termination reaction

$$\cdot C_2HCl_4 + \cdot Cl = C_2HCl_5$$

Vinyl Chloride

Schmitz & Schumacher[85] again obtained the same rate equation as for the other chloro olefines, provided the pressure of A was above 80 mm. The temperature coefficient gave $E_3 - \frac{1}{2}E_4 \sim 0$. However because of the extreme inhibition by oxygen they assumed

$$k_{ox}(O_2) >> k_3(Cl_2)$$

and concluded E_3 must be appreciable and $\geqslant$ 6 k. cal; which made $E_4 \geqslant$ 10 k. cal. This latter value was quite out of line with the usual assumption of $E_4 \simeq 0$ and it is obviously incorrect.

Two examinations of the vinyl chloride system were carried out by Dainton et al. by methods identical to those used for the trichloroethylene system. The same activated radical scheme was applied.

In the direct experiments the rate[48] was found to be so rapid that only four or five readings could be obtained during the linear portion of the pressure v time curve and several replicate runs had to be carried out in order to establish the rate accurately. The slight dark reaction was taken to be negligible.

Whilst the rate was independent of (A) at pressures above 130 mm, it had a dependency on $(A)^{\frac{1}{2}}$ for pressures of A between 10-35 mm. Rate determinations and sector measurements at 25 and 55°C using mixtures of 150 mm (A) and 50 mm Cl_2 allowed k_4 and k_3 to be obtained. $E_3 - \frac{1}{2}E_4$ gave a value of 780 cal which can be compared with Schumacher's value of

about zero. However E_3 was 900 cal.

Vinyl Chloride was also competed against cis 1.2 $C_2H_2Cl_2$[49]. The results showed that reactions α, β, and γ were probably also significant in this system. Again k_2/k_2 could not be evaluated explicitly but on the assumption that α, β and γ were not markedly structure dependent, E_2 for vinyl chloride was approximated to E_2 for cis dichloroethylene as before.

Ethylene

The study of this system by Dainton[48] and co-workers has already been mentioned. It was hoped that it would 'round off' the investigation of the chloroethylene chlorinations. Their study showed that for pressures of ethylene up to 70 mm, and of Cl_2 up to 60 mm, under which conditions, termination was thought to be by (5),

$$\text{i.e.} \quad \cdot ACl + \cdot Cl = ACl_2$$

the rate equation was of the form

$$R_p = k_o I_{abs}^{\frac{1}{2}} (C_2H_4)^{\frac{1}{2}} (Cl_2) / \left[a + b(Cl_2) \right]^{\frac{1}{2}}$$

$$\text{where} \quad a/b = k\alpha / (k\beta + k\gamma)$$

if the activated monochlorethyl radical was postulated. No sector or overall rate measurements were possible due to the complex rate expression.

Dark reaction in this system was found to be more marked than in the other systems being about 2% of the photo rate at the lowest intensities and pressures used. As in the case of vinyl chloride the photo rate was extremely rapid. The spread in measured rates at high intensity was $\pm$ 10%.

Monochloro-ethyl radical

An interesting investigation of the disproportionation and recombination reactions of the monochloro ethyl radical $\cdot C_2H_4Cl$

has recently been reported.

The method involved the generation of chlorine atoms by photolysis of either carbonyl chloride[87] or carbon[88] tetrachloride using a medium pressure mercury arc. In the CCl_4 system a gaseous mixture of ethylene and CCl_4 was allowed to mix for 30 minutes in a pyrex RV before photolysis. The reaction was studied at 26°, 76°, and 110°C. The main products were found to be 1.4 dichloro-butane: 1.3.3.3 tetrachloro-propane, $CHCl_3$, C_2Cl_6 and traces only of $C_2H_4Cl_2$, C_2H_5Cl and C_2H_3Cl. They found no evidence for excited $\cdot CCl_3$ or $\cdot C_2H_4Cl$ radicals. Reactions of interest with respect to the photochlorination of ethylene were included in their reaction scheme viz.

combination	$2C_2H_4Cl$	= $(C_2H_4Cl)_2$	(4)
Disproportionation	$2C_2H_4Cl$	= $C_2H_4 + C_2H_4Cl_2$	(a)
	$2C_2H_4Cl$	= $C_2H_5Cl + C_2H_3Cl$	(b)

The relative rates of these reactions were given by

$$k_4 \geqslant 10\ k_a \text{ or } 10\ k_b$$

It seems that the production of significant amounts of 1.3.3.3. tetrachloro-propane presumably by reaction

$$\cdot C_2H_4Cl + \cdot CCl_3 = C_3CC_2H_4Cl \qquad (e)$$

whilst only traces of $C_2H_4Cl_2$ were formed, requires some explanation. In fact they do not include the corresponding reaction

$$\cdot C_2H_4Cl + \cdot Cl = C_2H_4Cl_2 \qquad (f)$$

in their reaction scheme and must have assumed all the dichloroethane was produced by disproportionation (a).

The Arrhenius parameters for

$$\cdot ACl + \cdot Cl = ACl_2$$

in the case of trichloro-ethylene have been given as

$$\text{Log}_{10}A_5 = 10.85 \qquad ^{86}$$

$$E_5 = 1.0 \text{ k. cal.}$$

Now it does not seem reasonable to suppose the activation energy for the bulky $\cdot CCl_3$ radical addition would be much lower than that for the chlorine atom reaction but the $\cdot CCl_3$ radical would certainly be more capable of dissipating any excess energy present in the $\cdot C_2H_4Cl$ radical thus its reaction efficiency on collision would be higher than that for the chlorine atom. The fact that (f) did not occur to any great extent seems to imply, contrary to their conclusion, that excited chloro-ethyl radicals were in fact present.

Tetrachloro-ethylene

The C_2Cl_4 system has been studied by Dickinson & Carrico[89] and Shott and Schumacher[90]. Both yielded the rate equation

$$R_p = k\, I_{abs}^{\frac{1}{2}}\, (Cl_2) \text{ at } 40^\circ$$

and the latter work gave an overall activation energy of 7.4 k.cal. The quantum yield was only about 400 but the reaction was strongly inhibited by oxygen, a chlorine sensitized oxidation being observed. Dickinson noted the formation of hexachloroethane crystals on the RV walls at 40°C.

Goldfinger et al. have made a thorough study of this system directly[91, 20, 21], and also in competition[23]. The initial direct experiments gave rate expressions approximately dependent on $I_{abs}^{\frac{1}{2}}\, Cl_2^{3/2}$ at temperatures below 85°C and on $I_{abs}^{\frac{1}{2}}\, (C_2Cl_4)^{\frac{1}{2}}(Cl_2)^{3/2}$ at temperatures around 250°C.

In the second set of runs they studied both the tetrachloro-ethylene and the pentachloroethane systems. They considered that both reactions could be represented by the following scheme:

$$Cl_2 + h\nu = 2Cl\cdot$$

$$C_2HCl_5 + \cdot Cl = HCl + \cdot C_2Cl_5 \quad (2')$$

$$C_2Cl_4 + \cdot Cl = \cdot C_2Cl_5 \quad (2)$$

$$\cdot C_2Cl_5 + Cl_2 = C_2Cl_6 + \cdot Cl \quad (3)$$

$$\cdot C_2Cl_5 = \cdot Cl + C_2Cl_4 \quad (-2)$$

$$\cdot C_2Cl_5 + \cdot Cl = C_2Cl_6 \text{ or } C_2Cl_4 + Cl_2 \quad (5)$$

$$2C_2Cl_5 = C_2Cl_6 + C_2Cl_4 \quad (4)$$
$$\text{or } C_4Cl_{10}$$

Pressure changes and direct photometric measurement of the chlorine concentrations were used to follow the reaction rates up to 30% reaction. Depending on reaction concentrations mixing times of 5-25 minutes were allowed before photolysis. Allowance was made for the Draper effect[92].

Complex steady state equations were set up and by studying the reactions at different temperatures in steady light the values for the complex ratios $k_3/k_4^{\frac{1}{2}}$ (from both systems), and $k_3k_2^{\frac{1}{2}}/k_5^{\frac{1}{2}}k_{-2}^{\frac{1}{2}}$ (from the C_2Cl_4 system) were obtained. The former between 350° and 450°K and the latter between 390° and 560°K.

Further separate investigations[21] of these systems using the rotating sector technique gave absolute values for k_3, k_4 and the complex ratio k_5k_{-2}/k_2. They noted that when a new reaction vessel was used 'conditioning' was necessary before reproducible results could be obtained. No 'hot atom' effects were noted.

In yet another study[47], C_2Cl_4 was competed successively with C_2HCl_5, C_2H_6, CH_4, CH_3Cl, CH_2Cl_2 and $CHCl_3$. The C_2Cl_4/C_2HCl_5 system was complicated by the pressure maximum mentioned above in the trichloroethylene system. However by correct choice of reactant pressures they obtained runs in which the pressure remained stationary, under which

circumstances their equations gave

$$k_2k_3/k_{-2}k_2' = (C_2HCl_5)/(Cl_2)(C_2Cl_4)$$

In this way this complex ratio was between 385° and 490° and gave

$$\text{Log } k_2'k_{-2}/k_2k_3 = -3210/T + 4.99$$

The competitions with methane and the chloro-methanes were more straightforward and ratios k_2/k_2' were obtained. Knox[57] had already measured the absolute rate constants k_2' for hydrogen abstraction from methane and the chloromethanes on the hydrogen scale. (see p29). Goldfinger adjusted his absolute scale in order to give the smallest deviation from the values found by Knox and thus obtained a reasonably consistent set of values of k_2 for C_2Cl_4. The temperature independence of k_2 between 360 and 475°C gave $E_2 = 0$. The complex rate constant ratio k_{-2}/k_2k_3 was also obtained in this work.

A combination of complex rate constant ratios determined in the above two sets of experiments allowed k_{-2} and k_5 to be evaluated.

Fluoro ethylenes

The photochlorination of C_2F_4[93] and $C_2F_3Cl_2$[93, 94] have been studied and found to exhibit the characteristic high quantum yields and small temperature coefficients which have been observed throughout the chloro-olefines. The rates were given by $kI_{abs}^{0.67}(Cl_2)$ and $kI_{abs}^{\frac{1}{2}}(Cl_2)$ respectively and $C_2F_3Cl_2$ underwent a chlorine sensitized oxidation in the dark with emission of light. Hydrogen bromide was found to add to C_2F_4 under photolysis with light of wavelength >3000Å [95].

TABLE 1.1

Arrhenius parameters for the chlorination of the series $C_2H_{4-n}Cl_n$ (and CO)

Reaction	Reactant A											
	C_2H_4		C_2H_3Cl		$C_2H_2Cl_2$		C_2HCl_3		C_2Cl_4		CO	
	$Log_{10}A$	E	$Log_{10}A$	E	$Log_{10}A$	E	$Log_{10}A$	E	$Log_{10}A$	E	$Log_{10}A$	E
(2) $A + \cdot Cl = ACl$		2.0 *	10.3±0.6	1.5±1.0 o	10.3±0.4	1.2±0.7	10.3±0.6	1.5±1.0 o	9.2	0	$Log_{10}A_{-2}/A_2$ = 2.81	
	10.6±0.3	5.8±0.5					9.75±0.3	?				
(-2) $\cdot ACl = A + \cdot Cl$							13.7±0.5	20.4±1.0	12.8	16.8		6.3
(3) $\cdot ACl + Cl_2 = ACl_2 + Cl$			8.75±0.2	0.92±0.5	8.7±0.3	2.7±0.6	8.78±0.1	5.1±0.2	8.31	5.4	9.4	2.96
(4) $2\cdot ACl = (ACl)_2$			9.9±0.2	0.3±0.1	10.5±0.3	0.5±0.5	9.56±0.3	0.5±0.2	8.66	0.08		
(5) $\cdot ACl + \cdot Cl = ACl_2$							$Log_{10}k_5$ = 10.85±1.0		11.03	0.06	11.6	0.83

Units. $Log_{10}A$ is in litre $mole^{-1} sec^{-1}$, E is in k cal $mole^{-1}$.

Notes. * calculated from ref 68 on the basis of $Log_{10}A_2 = 10.3$

o Estimated, see text.

? Doubt as to whether any activation energy.

References	
(2)	68, 49, 39b, 49, 47+57, ..
This work,	, , 86, , 32.
(-2)	, , 86, 47 , 32.
(3)	, 48, 39b, 84, 21 , 32.
(4)	, 48, 39b, 84, 21 , .
(5)	, , 86, 47 , 32.

CHAPTER 2.

EXPERIMENTAL.

This chapter will be devoted to a general description of the techniques and equipment used in the present work. Modifications which were required for particular investigations will be described later in the relevant chapters.

2.1. APPARATUS

Kinetic System:- The high vacuum, static system shown in Fig. 2.1. was built from pyrex glass and was of conventional design except for the taps.

The use of conventional greased taps in kinetic studies suffers from two disadvantages. Firstly, and more importantly, large analytical errors can be incurred if the reaction products are soluble in the tap grease; and secondly reactants which are particularly reactive at room temperature, for instance halogens, will readily react with most greases and cause them to harden with the result that frequent regreasing is necessary. In this work two attempts were made to obviate these difficulties.

For the initial work on ethylene and isobutene (sections 3.1 and 3.3) 'EXELO' flat taps were used in all parts of the apparatus exposed to chlorine or reaction products. A diagram of the 'EXELO' tap is given in fig. 2.2. The contact surfaces of both top and bottom sections of the tap are flat and can be easily smoothed by polishing with a little jeweller's rouge. Only very small amounts of grease are therefore required for efficient lubrication and errors due to solution in the tap grease can be cut to a minimum. A halogen resistant

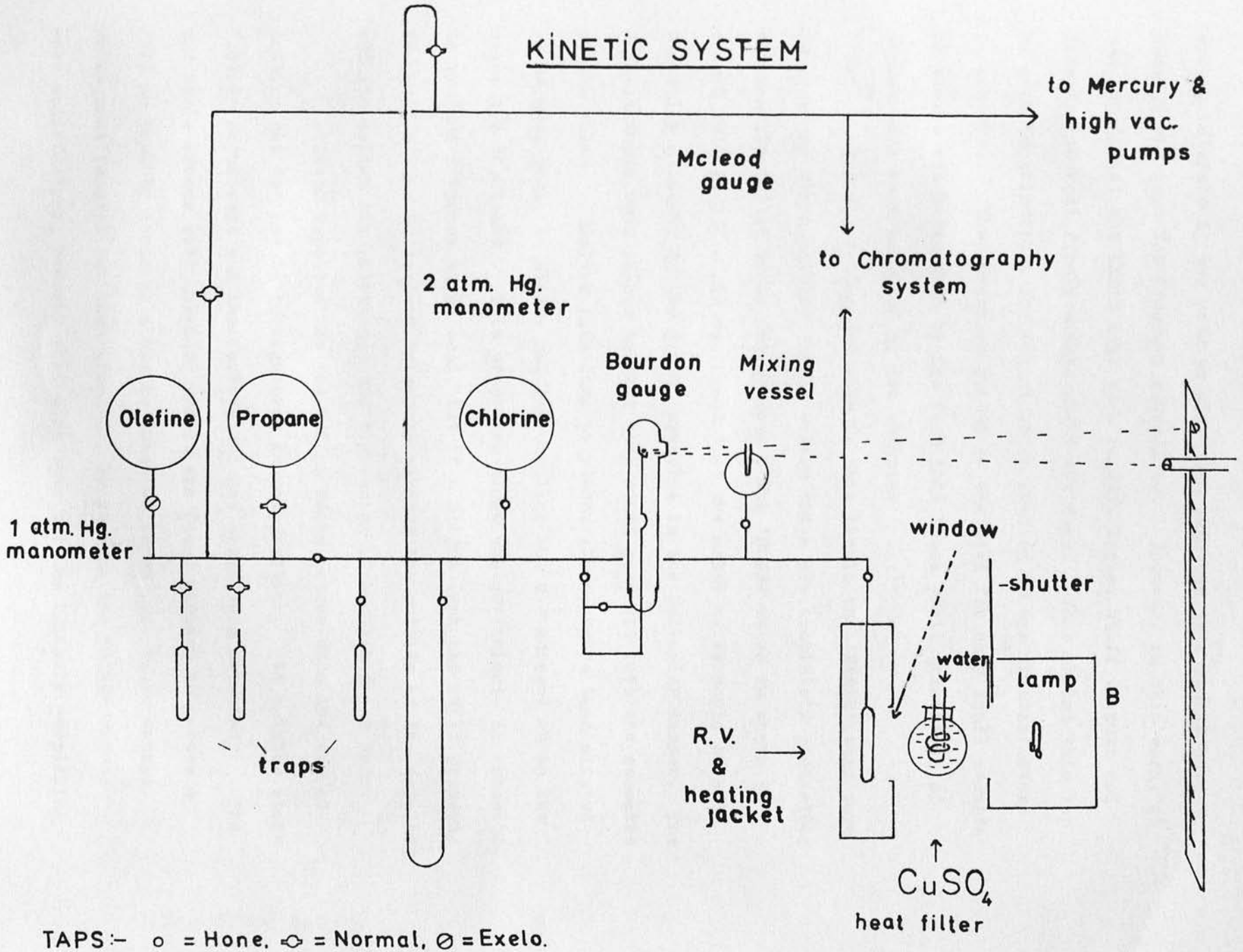

KİNETİC SYSTEM
to Mercury & high vac. pumps
Mcleod gauge
to Chromatography system
2 atm. Hg. manometer
Bourdon gauge
Mixing vessel
Olefine
Propane
Chlorine
1 atm. Hg. manometer
window
-shutter
water
lamp
B
traps
R. V. & heating jacket
CuSO4
heat filter
TAPS :- o = Hone, ⊂ = Normal, ⊘ = Exelo.

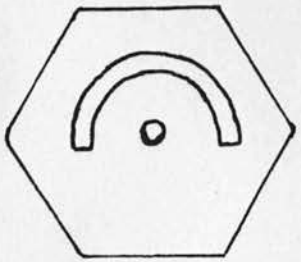
Fig 2.1

grease 'Florube A' was used on all these taps and this should have removed the need for frequent regreasing. However, in this work, it was found that the EXELO taps very rapidly became stiff to turn and finally 'locked' firmly within about six days. Thus whilst this tap is good in principle, for chlorination studies it was unsatisfactory in practice. The advantage gained by the need for only small amounts of grease was outweighed by the fact that these small quantities of grease were soon hardened by the chlorine.

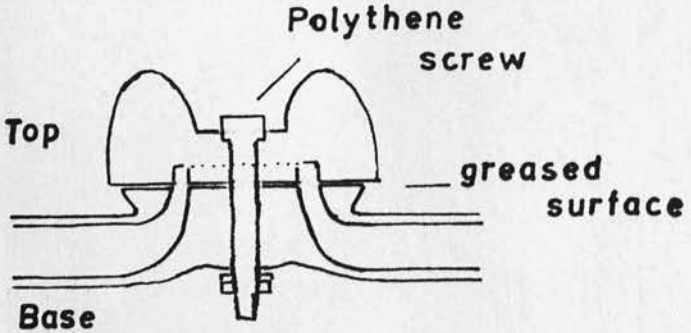
For all subsequent work in this thesis the 'EXELO' taps were replaced by chrome-nickel 'HONE' valves which are completely greaseless and contain teflon seats and glands. The 'HONE' valve is shown in detail in fig. 2.2. It was found that the metal valve could be successfully attached to the glass appartus in the following manner. The lead-in tubes were chosen so that they would just fit into the recesses on the valve. Quarter inch long polythene sleeves were then slipped on to each tube, as shown, and the coupling nut was screwed on to the valve and tightened. This procedure alone was sufficient, on occasion, to produce a vacuum tight seal, but if a slight leak was still present, it could always be removed by gently warming the outside of the coupling nut (to soften the polythene) and tightening it another $\frac{1}{2}$ - $\frac{3}{4}$ turn.

After repeated use the Teflon seats became worn and the adjusting nut 'A' had to be tightened in compensation. At a later stage further adjustment was ineffective and new seats were necessary. The old seats became well embedded and it was found easiest to secure a grip on them by screwing a coarse threaded screw into their centre. Subsequent removal was then simple. In general the 'HONE' valves were satisfactory, however when worn they had the initially perplexing

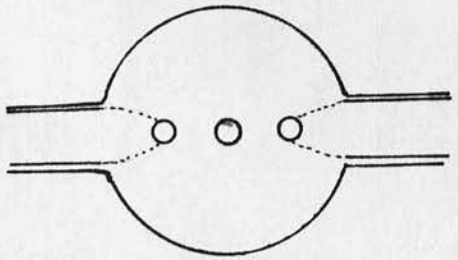
Exelo Tap



Top from below



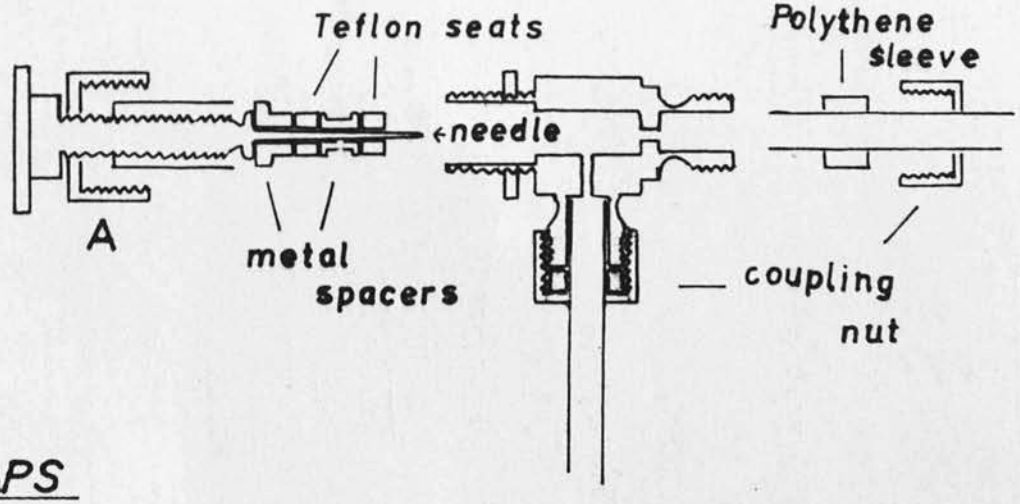
Side view



Base from above.

TAPS

Hone Valve



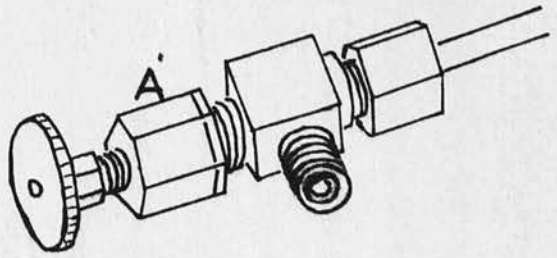


Fig 2.2

characteristic of leaking only when shut. A disadvantage in their use was that the usual high voltage discharge leak detector for glass systems, sparked on to the metal preferentially whenever it came within about eight inches of a tap and to obviate this some non conducting shield had to be employed. Shielding was difficult when the suspected leak was very near a tap.

In the non analytical sections of the kinetic system one EXELO tap was retained on the olefine storage bulb whilst all the other taps were of conventional design. In this case the EXELO tap was satisfactory as the storage-bulb-tap was not turned as frequently as those in the analytical section. All the conventional taps were greased with 'Apiezon L' (a hydrocarbon grease). This was found to be more satisfactory than silicone high vacuum grease for two reasons. The silicone grease tended to 'creep' down the glass tubes and produced devitrification if any subsequent glass blowing was carried out in an adjacent area. At the same time the gradual loss of grease from the tap, coupled with the hardening of the grease by chlorine, soon caused the tap to become difficult to turn. The more viscous Apiezon grease was not found to 'creep' appreciably unless heated, and it did not produce devitrification. Furthermore Apiezon greased taps could be maintained vacuum tight for as long as six months; gentle warming being sufficient to allow them to turn when the grease became hardened.

Evacuation:-

The kinetic system was evacuated by means of a standard mercury diffusion pump backed by a 'Speedivac' rotary oil pump. A two litre backing bulb was also included between the pumps, and a vacuum of 10^{-5} - 10^{-6} mm Hg could be obtained. Liquid nitrogen traps were

positioned before the mercury pump to stop chlorine and reaction products from destroying the mercury.

Pressure Measurement:-

Gas pressure measurements could be made on a glass spoon Bourdon gauge or on a mercury manonmeter. The Bourdon gauge was compared with the manometer and a calibration graph was drawn which showed the gauge to be three times as sensitive as the manometer up to a pressure of 8 cm. Hg. Oscillations of the Bourdon mirror, caused by vibration, made the gauge difficult to read initially. However it was found that application of a very thin coat of picien wax to the fine glass linkages holding the mirror, greatly reduced these oscillations, without significantly affecting the response of the gauge.

For later work at high pressures a second mercury manometer was built, which could read to two atmospheres pressure. Both this and the one atmosphere manometer had one limb made of capillary and when accurate pressure measurements were being taken allowance had to be made for capillary depression. The capillary depression was easily obtained by pumping out both limbs of the manometer under high vacuum.

The efficiency of evacuation was measured by means of a simple tilting McLeod gauge.

Mixing Vessel:-

The mixing vessel 'M' consisted of a 500 ml. globe with a small centrally placed heating element as shown. Thorough mixing was achieved by means of the convection induced by keeping the central element at around 60°C.

Illumination:-

Photolysis was achieved by light from either a 250 Watt

Tungsten filament lamp or a Hanovia 300 Watt U-shaped mercury vapour lamp. The lamps were placed about 20 cm. from the reaction vessel housed in a metal box 'B'. One side of the box could be slid upwards and acted as a shutter. The light passed through a 1 litre spherical flask containing a 10% copper sulphate solution; this acted as a heat filter and also roughly focussed the light on-to the reaction vessel. The copper sulphate solution was kept cool by means of a spiral tube through which cold water passed.

Reaction Vessel:-

Various reaction vessels were used, details will be given later. The usual volume was about 70 cc and the entire volume including the narrow bore lead-in tube was surrounded by a double walled glass cylinder. Between the walls of the cylinder was wound a wire heating element whose temperature could be varied by adjusting the voltage supplied to it from a multiterminal voltage stabiliser. Thermostatting was completed by wrapping several layers of asbestos rope round the entire heating jacket and finally covering this with layers of asbestos paper. The ends of the jacket were shut by $\frac{1}{2}$ inch thick asbestos blocks; the top block contained a small hole through which a thermometer was inserted. Temperatures were obtained with the tip of the thermometer in contact with the outside of the reaction vessel. A 'window' was finally cut in the asbestos insulation, such that the reaction vessel bulb could be exposed to illumination. The non-illuminated dead space was less than 1 cc.

Temperature control was normally to $\pm$ 1°C. However when the ultra violet lamp was used a very considerable amount of heat was generated in the lamp housing and a fast stream of cold air had to be blown through it in order to maintain a steady reaction vessel temperature.

Storage of Reactants:-

The purified reactants (see 2.3) were stored in 2 litre bulbs fitted with traps. At regular intervals these bulbs were checked for leaks by freezing down their contants and testing for any residual pressure. As the chlorine bulb was fitted with a metal tap it was not necessary to follow the usual procedure of keeping this reagent at liquid nitrogen temperatures.

Analytical System

Analysis of reaction products was carried out by means of gas phase chromatography. A schematic diagram of the system used is given in fig. 2.3.

Carrier gas:-

Cylinder hydrogen was used as carrier gas but it was first dried by passage through the tube 'c', containing activated Linde molecular-sieve. From time to time the sieve was reactivated by baking it in a metal crucible.

Flow Regulation:-

For operation of the chromatography columns at room temperature the conventional combination of mercury bubbler and baffle tubes was sufficient to produce a steady hydrogen flow. However the dichloride products formed by chlorine-olefine additions had relatively high boiling points and therefore at room temperature their retention times were much longer than those of the monochloro products. In order to reduce the overall analysis time and also produce reasonably sharp peaks for the high boiling fractions, the column had to be temperature programmed. The increase in viscosity of the hydrogen with rise in temperature must be counteracted by an increased input pressure to the column if a constant gas flow is to be maintained. For this reason

ANALYTICAL SYSTEM

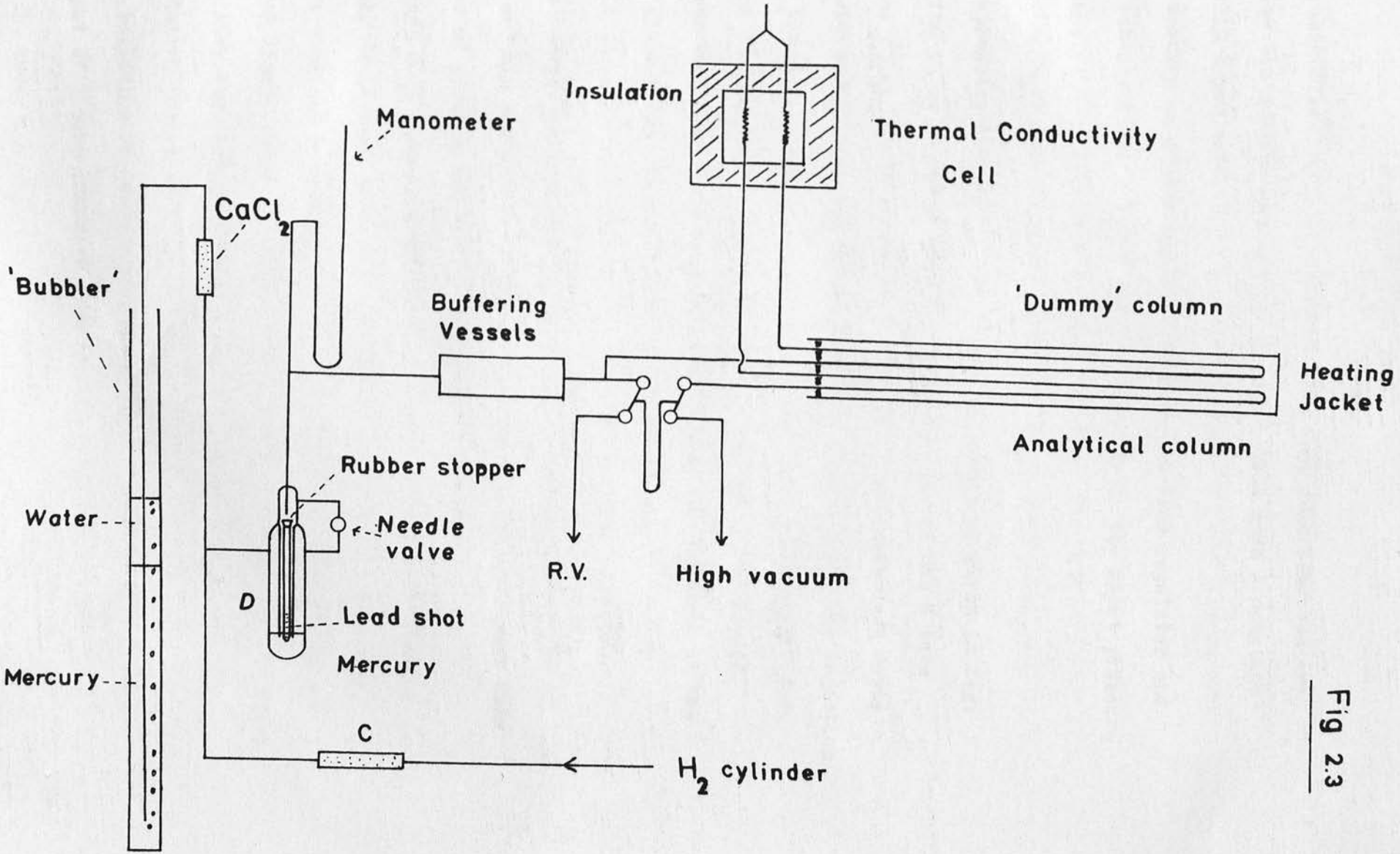


Fig 2.3

a simple float-valve[96] type of constant mass flow regulator was incorporated in the carrier-gas line as shown, D. This gave a constant flow to within 1 per cent.

A mercury monometer attached between the flow regulator and the baffle tubes allowed a rapid check to be made on the input pressure to the columns.

Injection:-

A schematic diagram of the injection system is given in fig. 2.3. Samples to be injected were first frozen down in the U tube under vacuum, using liquid nitrogen. With the liquid nitrogen dewar still in position hydrogen was then allowed to flow through the injection system into the column until the input pressure had nearly stabilised. Injection was finally accomplished by rapidly replacing the liquid nitrogen dewar by a beaker of warm water whereupon the contants of the U tube were flushed into the column by the carrier gas.

Columns:-

The chromatography system employed here required the use of one 'dummy' and one analytical column. All the columns used were made of 1.5 metres of pyrex glass tubing of internal diameter 2.3 mm. Column packings were made from 80-100 mesh celite coated with various liquid phases, which were carefully applied to give uniform coverage. These uniform coatings were obtained by dissolving the required weight of the desired liquid phase in carbon tetrachloride, adding the necessary amount of celite, and then pumping-off the CCl_4 under vacuum, whilst constantly shaking the mixture.

The following column packings were used. Percentages are in terms of weight of liquid phase, per weight of celite.

(1) 22% Dinonyl phthalate. For preliminary work on ethylene and isobutene (3.1, 3.3).

(2) 20% Dinonyl phthalate + 4% Ethylene glycol. For propene work (Chapter 4).

(3) 15% Butyl phthalate + 15% Ethylene glycol. For propene and ethylene work (4.5 and Chapter 5).

(4) $\frac{1}{2}$ column of (1) + $\frac{1}{2}$ column of (3). Final work on ethylene (Chapter 5).

For column (1) the flow rate for optimum operation was obtained from the Van Deemter equation[96] by plotting the height equivalent to a theoretical plate (HETP) against the flow rate in cc/min. A value of the flow rate near the minimum in the graph was chosen. The HETP was calculated from the following standard relationships.

$$\text{HETP} = \frac{\text{Column length}}{N}$$

N = No. of theoretical plates and is given by

$$N = 16\left[\frac{V_r}{w}\right]^2$$

where V_r is the true retention volume and w is the width of peak at base and is in the same units as V_r.

All the above columns were very similar in operation and further graphical determinations of optimum flow rate were not necessary. Any fall-off in efficiency was at once apparent in a loss of peak sharpness and the necessary adjustment of the flow rate was simple. The flow rates used were 18-20 ccs per minute and these were measured by means of a soap bubble flow meter.

The dummy and analytical columns were placed side by side in a double walled, electrically heated, glass jacket. For normal

runs the column temperature was kept about 35°C until products boiling below 73°C had been eluted. These products were usually iso and n-propyl chlorides and a little 2.2 dichloro propane, and their respective retention times were approximately 4½, 7, and 13 minutes. The voltage to the heating jacket was increased after the latter peak i.e. at about 14 minutes, and the column temperature rose to 70° or 80°C within half an hour. Retention times for further products would serve no useful purpose here as the rate of column heating was not determined accurately and varied somewhat with the room temperature. However it might be noted that the highest boiling major dichloride product analysed, namely 1.2 Dichloro isobutane Bpt. 106.5°C had a retention time around 45 minutes using the above procedure.

The orders of elution, from the different columns and the boiling points of the various products were as follows

Column (1)

(a) Iso propyl chloride, 36.5°C, (b) n propyl chloride, 46.4°C (c) 2.2 dichloropropane 70°C, (d) dimethyl vinyl chloride, 68°-69°C, (e) Methallyl chloride, 71°-74°C, (f) 1.2 dichloro ethane, 83.8°C, (g) 1.1. dichloro propane, 87°C, (h) 1.2 dichloro propane, 96°C, (i) 1.2 dichloro isobutane, 106.5°C.

Column (2)

(a), (b) + allyl chloride 45.7°C, (c), (g), (h).
one peak.

Column (3)

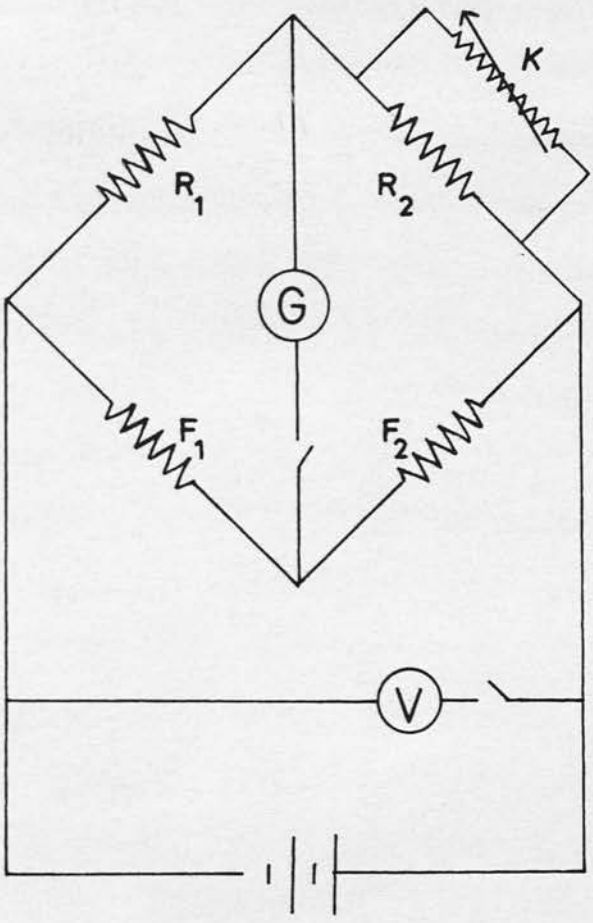
(a), (b), allyl chloride, (c), (g), (f), (h).

Column (4)

(a), (b), (c), (g), (f), (h). 1.1.2 trichloro ethane 114°C, 1.3 dichloro propane 120°.

Fig 2.4

Katharometer Circuit Diagram



2.2. Identification of Products and Quantitative Analysis

Identification of chromatographic peaks was usually accomplished by matching the retention times for the experimental products with those obtained for authentic, pure samples of the expected products. This was successfully carried out for n and iso propyl chloride, 1.2 dichloro propane, 1.2 dichloroethane, 1.2 dichloro isobutane and tertiary butyl chloride.

Adequate identification of the three secondary chlorination products of propane was obtained as follows. Chlorination of n propyl chloride yielded only three peaks which were, reasonably, taken to be the 1.1, 1.2 and 1.3 dichloro propanes. The respective boiling points of these substances namely 87°, 96° and 120° allowed no ambiguity over the order of elution and showed that the main products were the 1.1 and 1.2 dichloro derivatives. Iso propyl chloride was likewise chlorinated and yielded only two products which were taken to be 2.2 and 1.2 dichloro propane. The further fact that the retention times of the supposed 1.1, 2.2 and 1.2 dichloro peaks were found to match those obtained for the minor products of propane chlorination, was taken as conclusive evidence for correct identification.

Identification of the β,β dimethyl vinyl and methallyl products from the isobutene chlorination was more difficult. Reagent bottles of each substance contained comparable proportions of both chlorides and the intended major component was uncertain. However in spite of the narrow bore of the chromatography column it was found possible to use the column in a preparative manner. Chlorination of isobutene alone, followed by chromatographic separation of the products allowed the collection of samples of each peak for subsequent infra-red analysis. The sample collection was carried out

by means of a U tube (containing a small plug of celite in the bend of the U) through which the effluent from the katharometer was passed. When the required peak showed on the recorder a liquid nitrogen dewar was placed round the U tube. The dewar and U tube were subsequently removed together, when the sample had been collected. As the dimethyl vinyl, and methallyl peaks had similar retention times, to avoid contamination, only the first $\frac{3}{4}$ of the first peak and the last $\frac{3}{4}$ of the second peak were collected. Fractions collected in this way were rerun through the column and shown to contain only one component. They were subsequently introduced into a gas cell for infra red analysis. Comparison of the spectra so obtained, with those given in reference 97, identified and differentiated the two products. (Collections had to be repeated once or twice in order to obtain sufficient samples for IR analysis).

Quantitative Analysis

Peak areas measured by a planimeter, were used to evaluate relative product concentrations. To reduce errors the usual method adopted here was to trace round the peak five times, however for the very small peaks ten circuits were required.

The sensitivity of a Katharometer depends on the changes in specific heat and thermal conductivity of the gas passing the detector filament. Mole for mole the size of these changes vary from one substance to another and for accurate work the relative sensitivity of the katharometer towards different substances must be determined.

Procedure

Secondary propyl chloride was used as the reference standard. A mixture of secondary propyl chloride and some other reaction product was made up in the mixing vessel. After thorough mixing various sized

portions of the mixture were injected into the chromatography system. Measurement of the relative peak areas, coupled with a knowledge of the mixture composition allowed the sensitivity factor for the particular reaction product to be determined.

CALIBRATION TABLES

Mixture I

1.2 Dichloro propane/iso propyl chloride; 1.07 : 1 by mole.

Sample No.	Peak area ratio 1.2 DCP/SprCl	Calibration factor	
1	1.17	1.09	
2	1.21	1.13	
3	1.18	1.10	Mean = 1.11
4	1.20	1.12	

Mixture II

1.2 Dichloro ethane/iso propyl chloride; 0.96 : 1 by mole.

Sample No.	Peak area ratio 1.2 DCE/SprCl	Calibration factor	
1	0.92	0.96	
2	1.00	1.04	
3	0.99	1.03	Mean = 1.03
4	1.02	1.06	
5	1.02	1.06	

Mixture III

Dimethyl vinyl chloride/iso propyl chloride; 1.16 : 1 by mole.

Sample No.	Peak area ratio DMV/SprCl	Calibration factor	
1	1.26	1.09	
2	1.20	1.04	Mean = 1.06
3	1.28	1.11	
4	1.15	1.00	

Mixture IV

1.2 Dichloro isobutane/iso propyl chloride; 1.02 : 1 by mole.

Sample No.	Peak area ratio 1.2 DCIB/SprCl	Calibration factor	
1	1.01	0.99	
2	1.02	1.00	Mean = 0.99
3	0.99	0.97	

Isomeric substances were all taken to have the same sensitivity. All peak areas quoted throughout this thesis have been corrected using the following calibration factors

SUMMARY OF CALIBRATION FACTORS

Substance	Factor
n propyl chloride	1
iso propyl chloride	1
(Allyl chloride	1) *
1.2 $C_2H_4Cl_2$	1.03
1.2 1.1 $C_3H_6Cl_2$ 2,2	1.11

* assumed

Summary of Calibration factors continued

	Substance	Factor
	dimethyl vinyl chloride	1.06
	Methallyl chloride	
1.2	$C_4H_8Cl_2$	0.99

2.3. Materials

Purification: Reactants and additives were purified by successive trap to trap (acetone + CO_2 to liquid nitrogen) distillations. Between each distillation the substance was allowed to warm till liquid and then it was degassed under high vacuum. Four or five such sequences were sufficient to remove all water and air. However other trace impurities remained and may well have produced first order termination of reaction chains. As already stated this is not usually important in competitive systems.

Reactants

Propane, ethylene and chlorine were obtained from commercial cylinders and were all 98% pure.

Propene was prepared by dehydrating May & Baker iso propyl alcohol under reduced pressure, using phosphorous pentoxide. Any alcohol which distilled over was collected in an ice/salt trap whilst the propene, Bpt - 47°C, passed on to a trap surrounded by liquid nitrogen. The final product after purification as above was chromatographically pure.

Isobutene was obtained by dehydration of tertiary butyl alcohol using concentrated hydrochloric acid. A stream of nitrogen was used to carry the gas from the reaction flask through an ice trap to remove any alcohol and thence to an acetone/cardice trap where the isobutene, Bpt - 6.6°C, was collected. After distillation the olefine was found to be pure except for 0.8% of tertiary butyl chloride.

Materials used as additives or for identification purposes.

Methallyl chloride, dimethyl vinyl chloride and 1.2-

dichloro isobutane were obtained from bottles supplied by L. Light & Co. Ltd. All were impure each one containing quantities of the other two. The dichloride was satisfactorily purified by trap to trap distillations; whilst the unsaturates were separated and identified as described in 2.2.

1.2 dichloro ethane, cis dichloroethylene and iso and n propyl chlorides, were obtained from departmental ampoules and were 99% pure.

1.2 Dichloro propane, and tertiary butyl chloride were from BDH lab. reagent bottles and were found to be chromatographically pure.

Carrier Gas

Hydrogen was obtained from a B.O.G. cylinder.

Taps and Greases

The EXELO taps were made by W.G. Flaig & Co. London N.W.2., whilst the HONE valves were supplied by F.J. Hone Ltd., London, S.E.25

Silicone high vacuum grease was made by Edwards High Vacuum Ltd; Apiezon L grease by Metropolitan-Vickers Electrical Co. Ltd. and 'Florube' grease type A, was obtained from B.D.H.

2.4. General Procedure

Mixtures of propane and olefine were first prepared as follows:

The minor component was allowed into the evacuated mixing vessel (MV) to the required pressure measured on a mercury manometer. The MV tap was then closed and the contents of the line were either frozen back into the storage bulb or pumped off. A large pressure of the intended major component was then allowed into the line and subsequently shared with the M.V. As soon as the pressure had equilibrated, (usually within 3 sec.) the M.V. tap was shut and the final pressure in the line was recorded. The pressures of the two reactants in the M.V. were thus simply obtained. By knowing the relative volumes of the M.V. and the line it was possible to anticipate the pressure required in the line to give a certain total pressure in the M.V. Sufficient mixture was usually prepared to allow at least 20 runs to be carried out from one filling of the mixing vessels. Adequate mixing of the gases was accomplished within 30 minutes.

Before each run the vacuum line and reaction vessel were pumped out to 10^{-5} mm Hg. With both the mercury manometers shut, chlorine was admitted to the reaction vessel, the pressure being measured by the all glass Bourdon gauge. After complete evacuation of the line, mixture was allowed into it to a certain pressure which was either measured on the Bourdon or on a mercury manometer depending on the pressure (the pressure limit of the Bourdon was about 10cm). The mixture was subsequently shared with the reaction vessel in the same way as above. The pressures of chlorine used, were always much less than those of the hydrocarbons and the lead-in tube to the reaction

vessel was only 2-3 mm diameter, thus back diffusion of chlorine from the RV was unlikely in the short time required for pressure equilibration. In admitting the hydrocarbons to the RV it was possible once again to anticipate the necessary pressure in the line that would produce a certain required pressure in the RV. The following relationship was derived

$$P_1 = P_m S + P_x$$

where P_1 is the pressure of mixture required in the line (volume V_1), which will produce a pressure P_m of mixture in the RV (volume V_2), when the RV already contains a pressure P_x of chlorine. S is the volume ratio $(V_2 + V_1)/V_1$.

The exact procedures adopted for the carrying out of the reactions in the various systems studied in this thesis varied from case to case and will be considered in the relevant sections. However in all cases on completion of reaction the products were distilled into the chromatography U tube for subsequent analysis. IF all the products did not freeze down under liquid nitrogen, air must have been present and the reaction was rejected.

CHAPTER 3

Preliminary Results

3.1 The Competitive Chlorination of Ethylene

The 'product' form of the competitive method detailed in 1.4 was applied to the photo chlorination of ethylene-propane mixtures. It was hoped that as the rate constants (k_2') were known for chlorine atom attack on propane [44], the absolute rate constant for chlorine atom addition to ethylene (k_2) would be easily obtained. The theory indicates that the relative rate constants for these processes should be accurately given by

$$\frac{k_2'}{k_2} = \frac{(C_2H_4Cl_2)\ (C_3H_8)_m}{(C_3H_7Cl)\ (C_2H_4)_m} \qquad \text{I}$$

The concentration ratio in equation I was evaluated experimentally from the analytical results and the known initial reactant concentrations (see 1.4 and appendix C).

(As the direct application of the above type of equation to the olefine/propane systems has not been possible in this thesis, the experimentally determined concentration ratios will generally be denoted as $\zeta^{\text{olefine product}}_{\text{propane product}}$. For example in the ethylene case using the secondary position in propane as competitive standard the observed concentration ratios were

$$_{m \text{ or } i}\zeta^{DCE}_{spr} = \frac{(C_2H_4Cl_2)\ (C_3H_8)_{m \text{ or } i}}{(\text{sec } C_3H_7Cl)\ (C_2H_4)_{m \text{ or } i}}$$

where the subscripts m, or i indicate whether the calculation was made using mean, or initial, hydrocarbon concentrations).

It is apparent that before the experimental results can

be simply interpreted in terms of relative rate constants, equation I must be shown to be applicable. In the ethylene system Σ^{DCE}_{spr} will then equal k_2'/k_2. For this to be true Σ^{DCE}_{spr} must be shown to be independent of reactant concentrations at constant temperature. The preliminary investigation of this system was therefore directed towards observing the effect of varying hydrocarbon, and chlorine, concentrations.

All the reactions in this section were carried out at 35°C in a 70 ml cylindrical pyrex reaction vessel, and the tungsten lamp was used for photolysis.

The Effect of Varied Hydrocarbon Concentration

Experimental: The general procedure has already been outlined in 2.4. In these runs the RV was usually illuminated within 30 sec of the admittance of the hydrocarbon mixture and photolysis was continued for 20 minutes before the products were finally analysed. Analysis showed that 99% of the products were normal and sec. propyl chlorides, and 1.2 dichloroethane.

Results

Table 3.1 shows the results obtained for fourteen different ethylene/propane mixtures, where the mixture composition was varied from 1/1 to 10/1. The chlorine pressure was kept constant at 1.5 mm Hg for all runs whilst the total hydrocarbon pressure was varied from 11 mm to 199 mm. The corresponding graph given in Fig 2.1 shows that $m\,\Sigma^{DCE}_{spr}$ depends linearly on ethylene pressure, at least up to a pressure of 70 mm whereas variation of the propane concentration has no detectable effect. At pressures of ethylene above 7 cm slight curvature in the graph, indicates a tendency for $m\,\Sigma^{DCE}_{spr}$ to

become less dependent on (C_2H_4). It is realised that this curvature depends entirely on three points, however, the reproducibility was good in this series of experiments and the curvature is probably real.

The straight line portion of the graph has a slope = $0.068 cm^{-1}$ and gives a positive intercept at

$$m\overline{Z}^{DCE}_{spr} = 0.075$$

Values of k_{spr}/k_{ppr} are also given in table 3.1. (It is known that the competitive method applies in this case and yields real rate constant ratios[44]). Runs 4, 13c and 14c have particularly high values for this ratio whilst 12a has a low value. The remaining twenty four runs give a mean value of 1.20 with a probable error of $\pm$ 0.007. (Inclusion of the above four runs gives a mean value of 1.22 with a slightly larger probable error of 0.01.) Nelson[98] obtained the expression

$$k_{spr}/k_{ppr} = 0.70 \pm 0.01 \exp (320 \pm 10/RT)$$

for the temperature dependence of this rate constant ratio. At 308°K this yields a value of 1.18 $\pm$ 0.04 which agrees well with the value obtained here.

Effect of Varied Chlorine Concentration

A few preliminary runs, indicated that increasing the initial chlorine pressure above 1.5 mm Hg produced increasing amounts of secondary chlorination products mainly formed from the mono-chloro propanes. For these higher chlorine pressures, it was therefore desirable to be able to stop the reaction in an early stage before secondary chlorination became significant. This was attempted by using copper-bronze to remove the unreacted chlorine.

Experimental

As before, the hydrocarbon mixture was admitted to the reaction vessel containing the required pressure of chlorine. In most cases, the gases were then allowed to mix in the dark for 1-20 minutes before commencing the photolysis, the longer mixing times being allowed for the higher chlorine pressures. The subsequent photolysis times were also varied from 4-20 minutes, shorter exposure necessarily being given for the higher chlorine concentrations.

Removal of Excess Chlorine

At the required stage in the reaction the RV was opened to a tube containing very fine flakes of copper-bronze. The inlet to this tube was then closed and the gases remaining in the RV and line, were pumped off. After 5-10 minutes the contents of the copper-bronze tube were distilled into the chromatography U tube and analysed. Results obtained in this way were extremely erratic for runs at high chlorine pressures, although a certain upward trend in $\neg^{DCE}_{spr}$ with increased chlorine concentration was apparent.

It was thought at this stage that irreproducibility was due to incomplete removal of the excess chlorine, and several other methods were therefore tested. The main aim behind these methods was to ensure that sufficient copper-bronze surface, was exposed for removal of all the residual chlorine. Two of the methods that were tried involved drawing the products through a U tube containing a dispersion of copper bronze supported on either (a) celite or (b) small glass helices. In these cases all the chlorine was certainly removed but the values of $\neg^{DCE}_{spr}$ were still somewhat erratic and tended to be up to a factor of ten higher than was expected on the

basis of runs at lower chlorine pressures. This latter observation suggested that the reaction producing 1.2 dichloro ethane was surface catalysed, either by the copper-bronze or by the supporting media.

In the light of later results (see Chapter 5) which proved the presence of a 'dark reaction' in the ethylene system it was assumed that results from the above investigation, where reaction mixtures were allowed to stand in the dark for varied times before being photolysed, would not be capable of useful interpretation. However when a final analysis of this work was made it was found that a few of the above runs were meaningful. Certain of the runs at chlorine pressures up to 14 mm were carried out without allowing the reactants to stand in the dark for more than about 30 sec. The results from these runs are given in table 3.2. Two different ethylene propane mixtures of composition 1 : 2.3 and 1 : 3.2 were used but all runs were carried out at a pressure of 23.2 mm of ethylene. By using a tube containing only copper-bronze (first method given above) attempts were made to prematurely stop those reactions which initially contained more than 3.0 mm of chlorine. It can be seen from the table that this was not altogether successful; for example run 613 was so rapid that even though it was admitted to the copper-bronze after only three minutes, 100% of the chlorine was consumed and about 6% of the products were due to multiple chlorination of propane. (Multiple chlorination of propane refers here, to the sum of the 1.1, 1.2, and 2.2 dichloro propanes formed by secondary chlorination of the initially formed n and sec propyl chlorides). As this secondary chlorination occurred in several cases, despite the use of copper-bronze, it was necessary to take

it into account for valid interpretation of the results. Thus the concentration ratio $m\sum^{DCE}_{Tpr}$ was calculated, where Tpr refers to the total products from propane chlorination. Fig. 3.2 shows that $m\sum^{DCE}_{Tpr}$ depends linearly on chlorine pressures up to 14 mm.

Miscellaneous runs

On the basis of the chlorine and ethylene dependence lines obtained above it is possible to obtain the equation of a plane which will depict the dependence of $m\sum^{DCE}_{Tpr}$ on both chlorine and ethylene pressure, provided the separate dependencies are in fact linear. In order to obtain the equation of this plane it is first necessary to draw a line showing the dependence of $m\sum^{DCE}_{Tpr}$ on ethylene pressure. Such a line has in fact been drawn on Fig. 3.1 by making use of the value $k_{spr}/k_{ppr} = 1.20$.

Derivation of the Equation of the Plane

The graph (3.1) of $m\sum^{DCE}_{Tpr}$ v C_2H_4 has a gradient $m_1 = 0.037\ cm^{-1}$ (up to 7.0 cm of C_2H_4), whilst the graph (3.2) of $m\sum^{DCE}_{Tpr}$ v Cl_2 has a gradient $m_2 = 0.073\ cm^{-1}$.

The equation of the plane is of the form

$$m\sum^{DCE}_{Tpr} = m_1(C_2H_4) + m_2(Cl_2) + C$$

where C_2H_4 and Cl_2 are the initial reactant pressures in cm Hg. and C is the value of $\sum^{DCE}_{Tpr}$ where the plane cuts the vertical axis.

The two lines (3.1) and (3.2) intersect at a point where $C_2H_4 = 2.32$ cm., $Cl_2 = 0.15$ cm., and $m\sum^{DCE}_{Tpr} = 0.125$. This point must be on the plane therefore:-

$$m\sum^{DCE}_{Tpr} = 0.037 \times 2.32 + 0.073 + 0.15 + C = 0.125$$

$$\therefore \quad C = 0.028$$

Thus the equation of the plane is

$$10\ Xm\sum^{DCE}_{Tpr} = 0.37(C_2H_4) + 0.73(Cl_2) + 0.28$$

A few runs were carried out where both chlorine and ethylene pressures were varied. In table 3.3 the values of $10 \times \frac{DCE}{Tpr}$ calculated for these runs from the above equation, can be compared with the actual values obtained by experiment. The concentration ranges covered were rather limited, but the correlation between observed and calculated values is within the experimental error exhibited by the scatter of the points on the chlorine dependence graph, 3.2.

In conclusion, it can be said that $\frac{DCE}{Tpr}$ depends linearly on ethylene pressure up to 70 mm, and on chlorine pressure up to at least 14 mm whilst the concentration of propane is not important. It is therefore apparent that under the conditions used here the ethylene/propane system cannot be treated in terms of the simple competitive scheme implied by equation I.

TABLE 3.1

The Effect of Varied Hydrocarbon Pressure on $\sum_{spr}^{DCE}$

Temp = 35°C. Chlorine = 1.5 mm Hg.

Run No.	Mixture Composition mm Hg. C_2H_4	C_3H_8	Relative Peak Areas $C_2H_4Cl_2$	sPrCl	pPrCl	$10X\sum_{spr}^{DCE}$	k_{spr}/k_{ppr}
1a	29.3	5.5	322	208	172	2.74	1.21
1b	29.2	5.5	375	248	201	2.67	1.23
2	37.9	8.9	385	254	212	3.43	1.20
3a	54.0	9.6	361	135	113	4.62	1.20
3b	29.0	5.2	301	191	153	2.64	1.25
4	43.1	24.0	226	336	237	3.68	1.42
5	44.7	30.8	188	323	292	3.94	1.11
6	24.3	4.2	314	209	173	2.38	1.21
7	8.2	6.3	68	375	321	1.35	1.17
8a	50.7	17.8	243	200	170	4.18	1.18
8b	27.3	9.6	199	250	215	2.66	1.16
8c	14.9	5.3	149	285	230	1.67	1.24
9	34.1	12.6	216	251	211	2.98	1.19
10a	7.5	8.4	46	385	310	1.31	1.24
10b	5.1	5.8	41	401	334	1.10	1.20
11a	69.9	7.4	574	114	95	5.23	1.20
11b	48.1	5.1	512	132	109	3.96	1.21
11c	32.8	3.5	414	140	110	2.94	1.27
11d	22.6	2.4	350	142	116	2.32	1.22
12a	41.3	4.6	413	114	106	3.84	1.08
12b	41.2	4.6	400	128	114	3.32	1.12
12c	39.5	4.3	377	120	108	3.24	1.11

TABLE 3.1 (continued)

Run No.	Mixture Composition mm Hg. C_2H_4	C_3H_8	Relative Peak Areas $C_2H_4Cl_2$	sPrCl	pPrCl	$10X \sum^{DCE}_{spr}$	k_{spr}/k_{ppr}
13b	48.5	4.7	461	105	84	4.09	1.25
13c	24.4	2.4	311	127	90	2.14	1.41
14a	145.4	53.7	252	95	77	9.78	1.23
14b	98.4	36.3	313	160	138	7.17	1.16
14c	9.1	3.3	78	197	142	1.19	1.39
14e	28.4	10.5	175	229	194	2.70	1.18

Note: In the above table and throughout the following tables peak areas are only consistent within each run where their relative values are in terms of moler ratios. No attempt has been made to allow for sensitivity-range changes from one run to the next, except where this is obviously necessary for the interpretation.

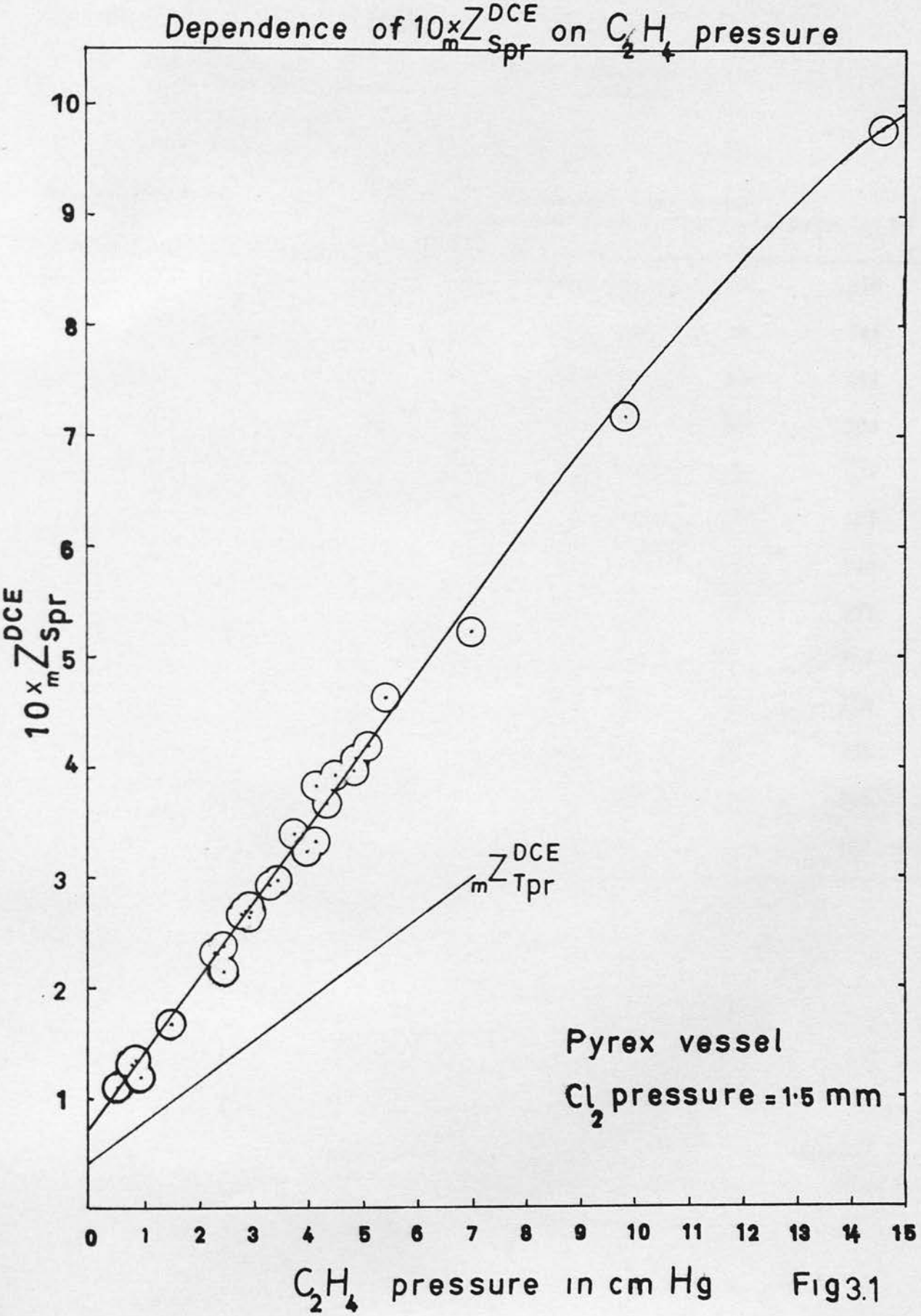

Dependence of $10 \times {}_{m}Z^{DCE}_{Spr}$ on C_2H_4 pressure
$10 \times {}_{m}Z^{DCE}_{Spr}$
${}_{m}Z^{DCE}_{Tpr}$
Pyrex vessel
Cl_2 pressure = 1·5 mm
C_2H_4 pressure in cm Hg

Fig 3.1

TABLE 3.2

Dependence of $_{m}\Sigma^{DCE}_{Tpr}$ on Chlorine pressure.

Temp = 35°C. C_2H_4 = 2.32cm Hg.

Run	Reactants in mm Hg Cl_2	C_3H_8	% Cl_2 consumed	Relative Peak Areas $C_2H_4Cl_2$	sPrCl	pPrCl	Multiple Pr	Total Pr	$10X_{m}\Sigma^{DCE}_{Tpr}$
Cl 1	7.6	7.5	80	228	166	131	21	318	1.88
2	1.5	"	100	155	198	146	2	346	1.36
3	9.0	"	100	363	240	172	45	457	1.87
4	13.5	"	90	554	300	200	84	584	2.04
5	10.5	"	82	336	248	164	40	452	1.77
6	4.5	"	33	220	232	180	11	423	1.59
7	0.5	5.4	100	71	80	66	-	146	1.11
8	2.5	"	100	465	431	348	18	797	1.19
9	2.3	"	100	425	413	326	22	761	1.14
10	2.0	"	100	354	308	240	10	558	1.33
15	6.5	"	83	225	140	113	15	268	1.51
16	1.0	"	100	170	178	140	-	318	1.18
18	1.5	"	100	232	227	180	5	412	1.21

TABLE 3.3

Miscellaneous Runs at Varied Chlorine and Ethylene Pressures

Run	Reactants in mm Hg			% Cl_2	Relative Peak Areas		$10X_m \sum_{spr}^{DCE}$	
	Cl_2	C_2H_4	C_3H_8	consumed	$C_2H_4Cl_2$	Total pr.	observed	calculated
2	4.50	30.8	11.4	73	128	243	1.80	1.75
3	0.22	50.0	13.5	100	502	653	2.08	2.15
4	6.10	20.6	7.6	87	194	407	1.40	1.48
5	6.20	25.4	6.9	93	252	397	1.47	1.67
7	0.71	47.8	11.2	100	185	212	2.08	2.10
8	2.58	30.3	7.1	100	131	171	1.64	1.59
9	3.88	34.8	7.8	74	146	179	1.67	1.85
10	2.46	39.8	9.3	70	408	519	1.76	1.93

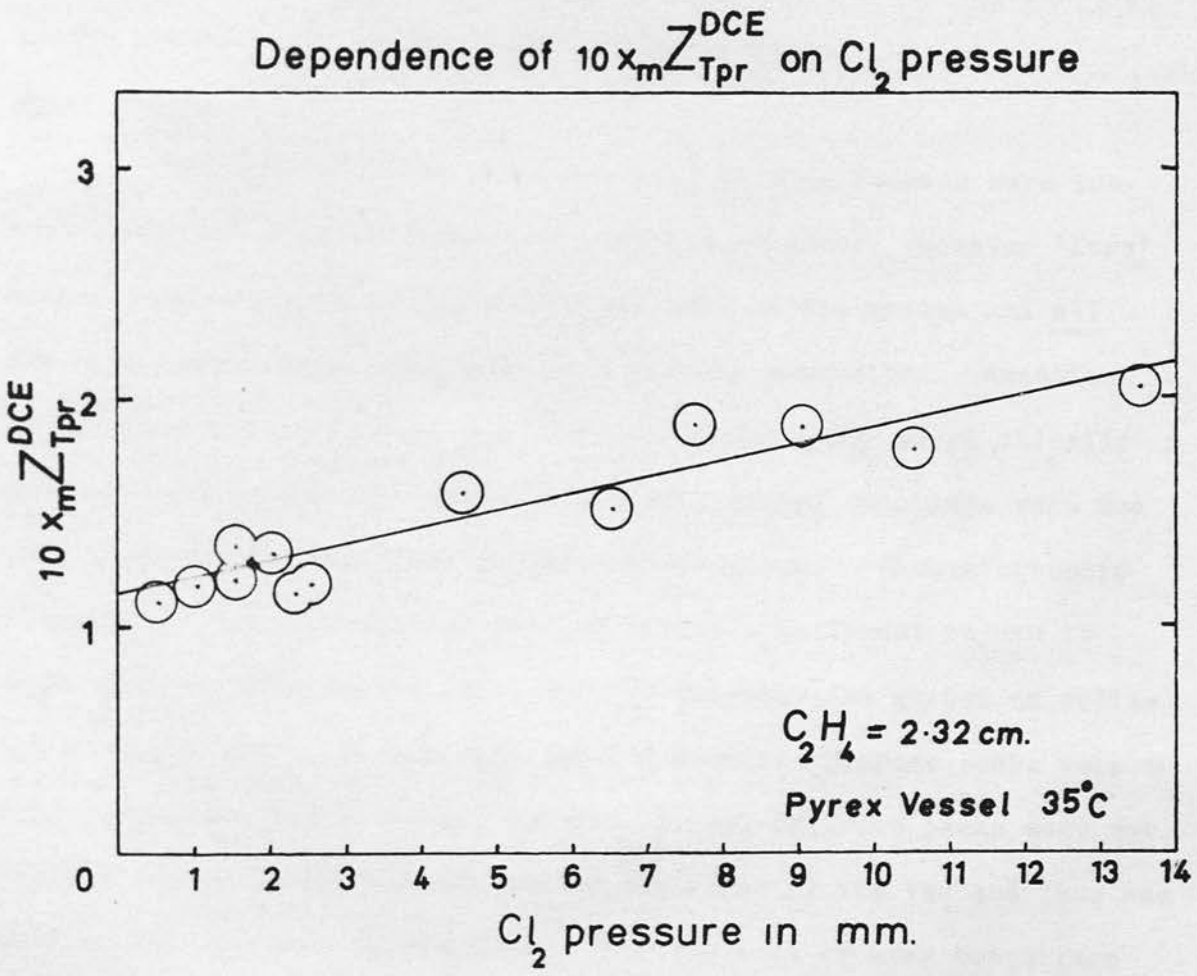

Dependence of $10 x_m Z^{DCE}_{Tpr}$ on Cl_2 pressure
$10 x_m Z^{DCE}_{Tpr}$
Cl_2 pressure in mm.
C_2H_4 = 2·32 cm.
Pyrex Vessel 35°C
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Fig 3.2

3.2 The Competitive Chlorination of Propylene

For the sake of continuity it is necessary at this stage to introduce some unpublished work which was carried out in this department by Miss E.M. Thomson. Towards the end of the investigation reported in 3.1 Miss Thomson performed some preliminary experiments on the chlorination of propylene/propane mixtures.

Experimental

The apparatus and procedure used by Miss Thomson were substantially the same as those used here for ethylene; however 'Hone' valves were employed in the analytical part of the system and all pressure measurements were made on a mercury manometer. Reaction of chlorine with propylene was found to produce only allyl chloride and 1.2 dichloropropane, whilst n and sec. propyl chlorides were the only products observed from propane chlorination. Chromatographic analysis of the products was carried out on a different column to those used in this thesis (viz. 20% w/w Polyethylene glycol on celite) and although the allyl chloride and 1.2 dichloro propane peaks were well separated, the n. propyl and sec. propyl chloride peaks were not. However the n. propyl was the better separated of the two and thus was used as the competitive standard. For the sake of easy comparison with other work in this thesis, Miss Thomson's results have here been converted into terms of sec. propyl chloride as competitive standard by using $k_{spr}/k_{ppr} = 1.20$. Furthermore as chromatographic detection was by means of a similar katharometer to the one used for this thesis, the calibration factors given on page 72 have been applied throughout.

Reactions were carried out in a 100 ml pyrex reaction vessel which was thermostatted at 42°C by being surrounded by a vapour

bath containing boiling methylene chloride. The reactants were allowed to stand in the dark for only a short time, before being photolysed for 20-25 minutes using a 300 watt tungsten lamp.

Here as in the previous case for ethylene, before the simple competitive theory could be applied to obtain k_2 for propylene, it was necessary to ascertain that ζ^{DCE}_{prCl} was independent of relative reactant concentrations. For this system, where the percentage consumptions of each hydrocarbon were similar, and small, and no secondary chlorination was detected, the concentration ratio $i\zeta^{DCE}_{spr}$ gave good accuracy.

Dependence of $i\zeta^{DCP}_{spr}$ on hydrocarbon pressure

Using a constant chlorine pressure of 2 mm Hg, three different mixtures of composition 1 : 1, 1 : 3 and 3 : 1 were investigated. Table 3.4 and Figs. 3.3 and 3.5 depict the results obtained. It can be clearly seen from Fig. 3.3 that for each individual mixture $i\zeta^{DCP}_{spr}$ varies linearly with propylene pressure whilst the gradients of the lines obtained increase with increase in the proportion of propane in the mixture. All three lines intersect on the ζ axis at a value of 0.85 which is some eleven times larger than the corresponding value found for ethylene. At the same time it can be seen from fig. 3.5 that the three different mixtures all show the same linear dependence on total hydrocarbon pressure, the composite line having a slope of 0.2 cm^{-1}. Fig. 3.5 also shows that $i\zeta^{Allyl}_{spr}$ is virtually independent of pressure and it seems likely that in this case the intercept value of 0.50 is a true measure of k_{allyl}/k_{spr}.

Dependence of $i\zeta^{DCP}_{spr}$ on Chlorine Pressure

The chlorine pressure was varied from 0.7-5 mm for runs

containing 55.5 mm of a 1 : 1 hydrocarbon mixture. Secondary chlorination was not important and therefore the reactions were allowed to proceed to completion. Table 3.5 and fig. 3.4 show that over this range of chlorine pressures the concentration ratio for dichloro propane is independent of halogen pressure. The corresponding values for the formation of allyl chloride were unfortunately not reported in this work.

It is therefore apparent that the propylene/propane system also cannot be treated in terms of the simple competitive theory.

TABLE 3.4

Pressure Dependence of $i\angle^{DCP}_{spr}$ at 42°C. Cl_2 = 2mm.

(Miss E.M. Thomson)

Run	Reactants in mm Hg		Relative Peak Areas			k_{allyl}/k_{spr}	$i\angle^{DCP}_{spr}$
	$C_3H_6 + C_3H_8$	C_3H_6	sPrCl	Allyl Cl	1.2 $C_3H_6Cl_2$		
Pr 2	76.0	38.0	171	74	390	.43	2.29
3	53.5	26.8	199	89	356	.45	1.79
4	38.0	19.0	206	86	288	.42	1.39
5	29.0	14.5	199	88	263	.44	1.32
6	16.3	8.2	244	117	284	.48	1.17
7	184.0	48.5	178	36	296	.57	4.66
8	132.0	34.8	156	31	161	.55	2.89
9	94.0	24.7	286	50	254	.49	2.48
11	48.0	12.6	260	45	178	.48	1.92
12	34.0	9.0	215	41	132	.53	1.72
13	228.0	171.0	34	60	551	.59	5.44
14	162.5	122.0	38	60	474	.53	4.16
15	116.0	87.0	35	55	305	.52	2.92
16	83.0	62.1	48	70	377	.49	2.65
17	59.0	44.1	73	98	406	.45	1.86
18	42.0	31.4	75	108	373	.49	1.68
19	21.0	15.7	64	100	263	.53	1.38

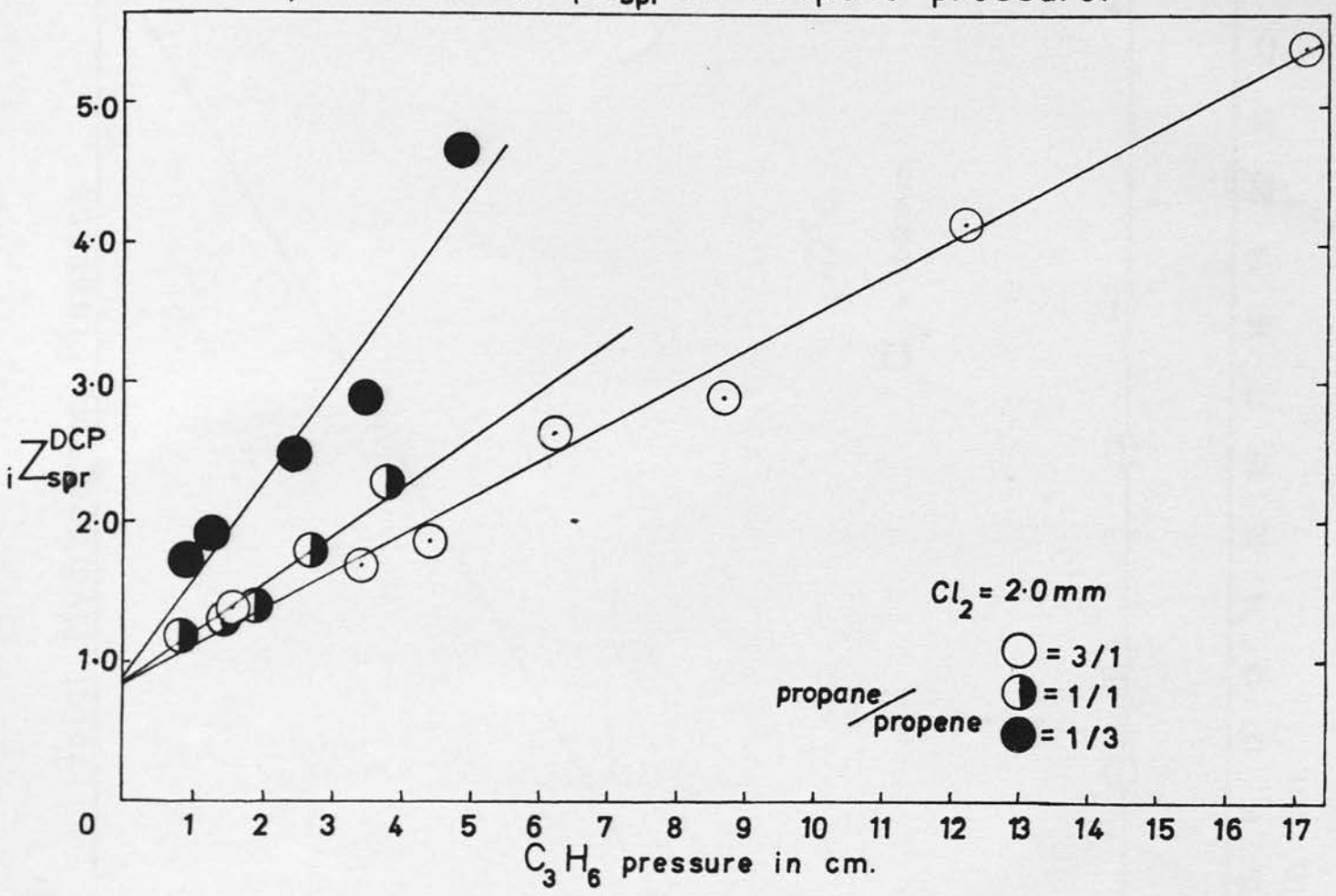
TABLE 3.5

Chlorine Dependence of $i\bar{Z}^{DCP}_{spr}$ M = 55.5 C_3H_6 = 27.8mm

Run	Cl_2 mm	s Pr Cl	1.2 $C_3H_6Cl_2$	$i\bar{Z}^{DCP}_{spr}$
21	1	35	38	1.09
3	2	199	356	1.79
23	3	287	560	1.95
25	4	350	764	2.18
24	5	542	1005	1.85
26	0.7	364	789	2.17

Fig 3.3

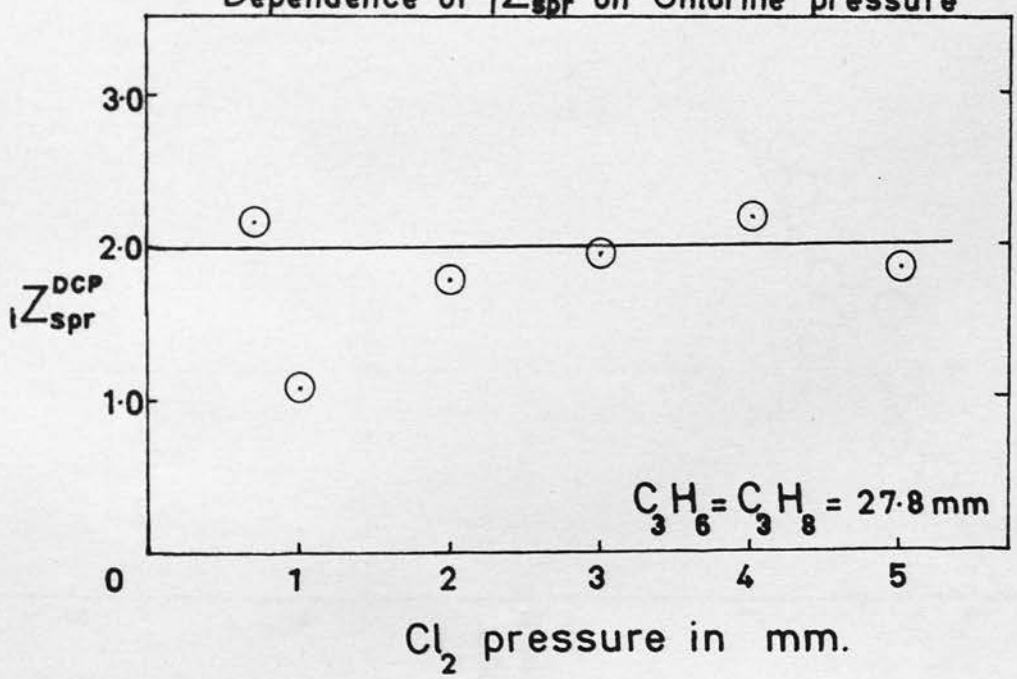
Dependence of $_iZ^{DCP}_{spr}$ on Propene pressure.



42° C.

Fig 3.4

Dependence of $_iZ^{DCP}_{spr}$ on Chlorine pressure



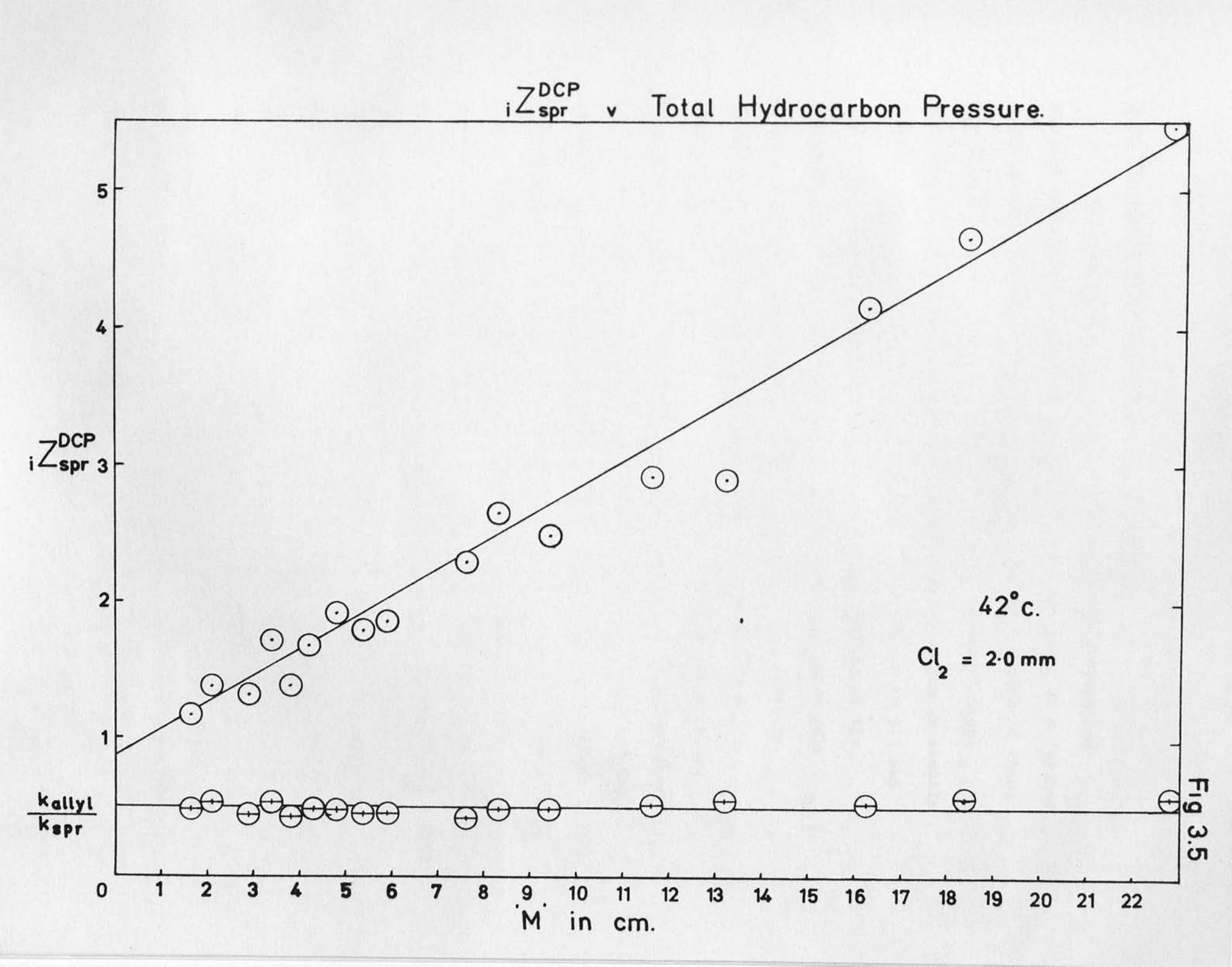

$_iZ^{DCP}_{spr}$ v Total Hydrocarbon Pressure.
$_iZ^{DCP}_{spr}$
$\frac{k_{allyl}}{k_{spr}}$
42°c.
Cl_2 = 2·0 mm
'M' in cm.
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

Fig 3.5

3.3 THE COMPETITIVE CHLORINATION OF ISOBUTENE

In view of the fact that both ethylene and propene had yielded unexpected results it was thought that the study of a further olefine system might either, establish the eccentric nature of these reactions, or yield results capable of a simple interpretation. Accordingly the isobutene:propane system was studied using an exactly similar procedure to that of the previous investigations in 3.1 and 3.2. It should be emphasised here that the realisation of the presence of a "dark reaction" in the ethylene system, which subsequently allowed the successful interpretation of the chlorine dependence in 3.1 did not come about until the end of these preliminary studies. Thus the investigation of the isobutene system was carried out in ignorance of the possible presence of a significant dark reaction and consequently the procedure used in 3.1 was adopted, reaction mixtures usually being allowed to stand in the dark before photolysis.

The chlorination of isobutene was found to yield three products. These were identified as described in section 2.2 as Methallyl chloride $ClCH_2-\underset{CH_3}{C}=CH_2$, $\beta\beta$ dimethyl vinyl chloride $CH_3-\underset{CH_3}{C}=CHCl$ and 1.2 dichloro isobutane. Slight traces of tertiary butyl chloride may also have been produced but these, if present, were small enough to be obscured by the 0.5% impurity of tertiary butyl chloride already in the isobutene. (see 2.3)

A large number of isobutene:propane mixtures of different composition were used to carry out the initial investigation into the presence or absence of a pressure dependence for the formation of 1.2

dichloro isobutane. It was soon apparent that the results were extremely irreproducible with a tendency to give very high values. (A more detailed account of this irreproducibility will be given shortly). However out of a mass of data a few runs gave values of $\sum_{spr}^{DCIB}$ much nearer to what one might have expected on the basis of the previous investigations on ethylene and propene; these results are reported below.

Dependence on hydrocarbon pressure

All runs were carried out using 1.5mm of chlorine. The results are shown in Table 3.6 and graphs of ${}_m\sum_{spr}^{MA}$, ${}_m\sum_{spr}^{DCIB}$ and ${}_m\sum_{spr}^{DMV}$ v Total hydrocarbon pressure are given in fig. 3.6 The 'scatter' of the points is quite large for all those graphs although it is proportionally worse in the case of the unsaturated products. It does however appear that the concentration ratios for all the products of isobutene chlorination, are dependent on total hydrocarbon pressure. The line for the additional reaction gives an intercept with the Z axis of 1.8 and a gradient of 0.76 cm^{-1}. This intercept value is about twice that obtained for propylene and twenty four times that obtained for ethylene, whilst the gradient is almost four times larger than that of the corresponding line for propylene.

Whilst the results in general cannot be regarded as precise there can be no doubt that at pressures about 1cm., more methallyl chloride is formed from isobutene than any other product and the percentage increases with pressure. On the other hand the reaction forming BB dimethyl vinyl chloride is much less significant and in fact, in certain random cases, it did not take place at all. It is possible however, that this product is formed by dehydrochlorination of the initially formed 1.2 dichloro-isobutene.

Irreproducibility

As already stated many other runs were carried out whose results are not presented here. All these runs gave extremely high values for the three $\sum$s but $\sum_{spr}^{MA}$ and $\sum_{spr}^{DMV}$ varied proportionally more than $\sum_{spr}^{DCIB}$, sometimes increasing by a factor three or four times larger than that for $\sum_{spr}^{DCIB}$. For any one run the Zs for the two unsaturates did not however increase by the same factor.

In many other cases no propyl chlorides were obtained at all; a few examples of such runs are given in Table 3.6 and in the test below. There was no correlation between mixtures compositions or pressures which produced these results as very often a mixture which would yield propyl peaks on one occasion, would not yield them on another. It is considered that the following observations explain the majority of these irregularities.

The analysis of four runs using identical reactant pressures are presented below:

Cl_2 = 1.5mm. C_3H_8 = 9.7mm. C_4H_8 = 2.6mm. T = 35°C.

Analysis

Run	sPrCl	pPrCl	D.M.vinyl Cl	Methallyl Cl	1.2 DCIB
B6(a)	40	33	51	480	104
(b)	None	None	54	523	98
(c)	None	None	54	494	101
(d)	89	81	25	378	116

Runs (a) and (d) were photolysed for 20 minutes.

Run (b) was left in the dark for 10 minutes before photolysis
Run (c) was left in the dark for 10 minutes and then analysed.

All runs and analyses were carried out in a completely darkened room.

It can be seen that runs (b) and (c) gave almost identical results and no propyl peaks were observed. One can conclude from this that complete reaction took place in the dark within 10 minutes and only isobutene and chlorine were involved.

Except for the dichloro product runs (a) and (d) give entirely different results. The only accountable difference in procedure between these two runs was that, having allowed the hydrocarbons into the RV, (a) stood for a slightly longer time before photolysis, than did (d). The time intervals involved cannot be given a precise value but they certainly differed by less than one minute. This was apparently quite long enough to more than halve the amount of propyl chlorides produced and the Z ratios thus differ by more than a factor of two for the 'identical' runs. In fact from (d) to (a) Z_{spr}^{MA}, Z_{spr}^{DMV} and Z_{spr}^{DCIB} increase by factors of 2.8, 4.5 and 2.0 respectively.

It appeared from the above that a very rapid 'dark reaction' occurred between chlorine and isobutene but it was thought possible that some of this reaction might have taken place in the liquid phase when the products were being frozen prior to analysis. This possibility was checked as follows.

A mixture of 16.2mm C_4H_8 and 17.6mm C_3H_8 was allowed to react with 1.5mm of chlorine in complete darkness for approximately

15 minutes. A small sample (1) of the reaction mixture was then admitted to chromatography U tube and analysed without freezing it down first. (This only led to a slight loss of peak sharpness). After a further few minutes a second, equivalent sample (2) was removed from the RV but this time it was frozen down as usual before analysis. Finally the RV was illuminated for 20 minutes to ensure all the chlorine had reacted and the residual contents (3) were analysed in the usual manner.

Run B (25)		tBuCl	D.M.vinyl Cl	Methallyl Cl	1.2 DCIB	
15 min dark	(1)	16	15	138	26	Not frozen
20 min dark	(2)	15	14	131	24	Frozen
20 min dark + 20 min light	(3)	20	20	175	35	Frozen

As the tertiary butyl chloride was only present as an impurity in the isobutene it can be used as a 'marker' and the following ratios will give an indication of any change in the relative amounts of the various products brought about by the different treatments.

	DMV / tBuCl	MA / tBuCl	DCIB / tBuCl
(1)	0.94	8.6	1.62
(2)	0.93	8.74	1.60
(3)	1.00	8.75	1.70

It can be concluded from the above that the 'dark reaction' does in fact take place in the RV and is not due to freezing down the reactants. In (3) photolysis appears to have increased the amount of chloride produced but these variations are probably

within the experimental error.

It is interesting to note that for those runs where no propyl chlorides were produced the relative amounts of the products are very nearly constant. The percentage yields are given below.

Run	% DMV	% MA	% DCIB	
B 6(b)	8.0	77.5	14.5	
6(c)	8.3	76.0	15.6	Dark only
5(20)	8.0	78.0	14.0	
5(22)	8.6	75.5	15.8	
B25(1)	8.4	77,0	14.5	Dark only

These values can be compared with those given in ref. 74 for the gas phase chlorination of isobutene alone at 0°C without photolysis. viz.

2.5 83.4 13.4 + 0.7% of tBuCl.

and also the corresponding reaction in the liquid phase, (ref. 74) viz.

3.0 87.0 9.0 + 1.0% of tBuCl.

A combination of all these results with the pressure dependence lines given in fig. 3.6 shows that the preferential formation of methallyl chloride is favoured by increased pressure, lower temperature, or change in phase from gas to liquid. These three observations concur.

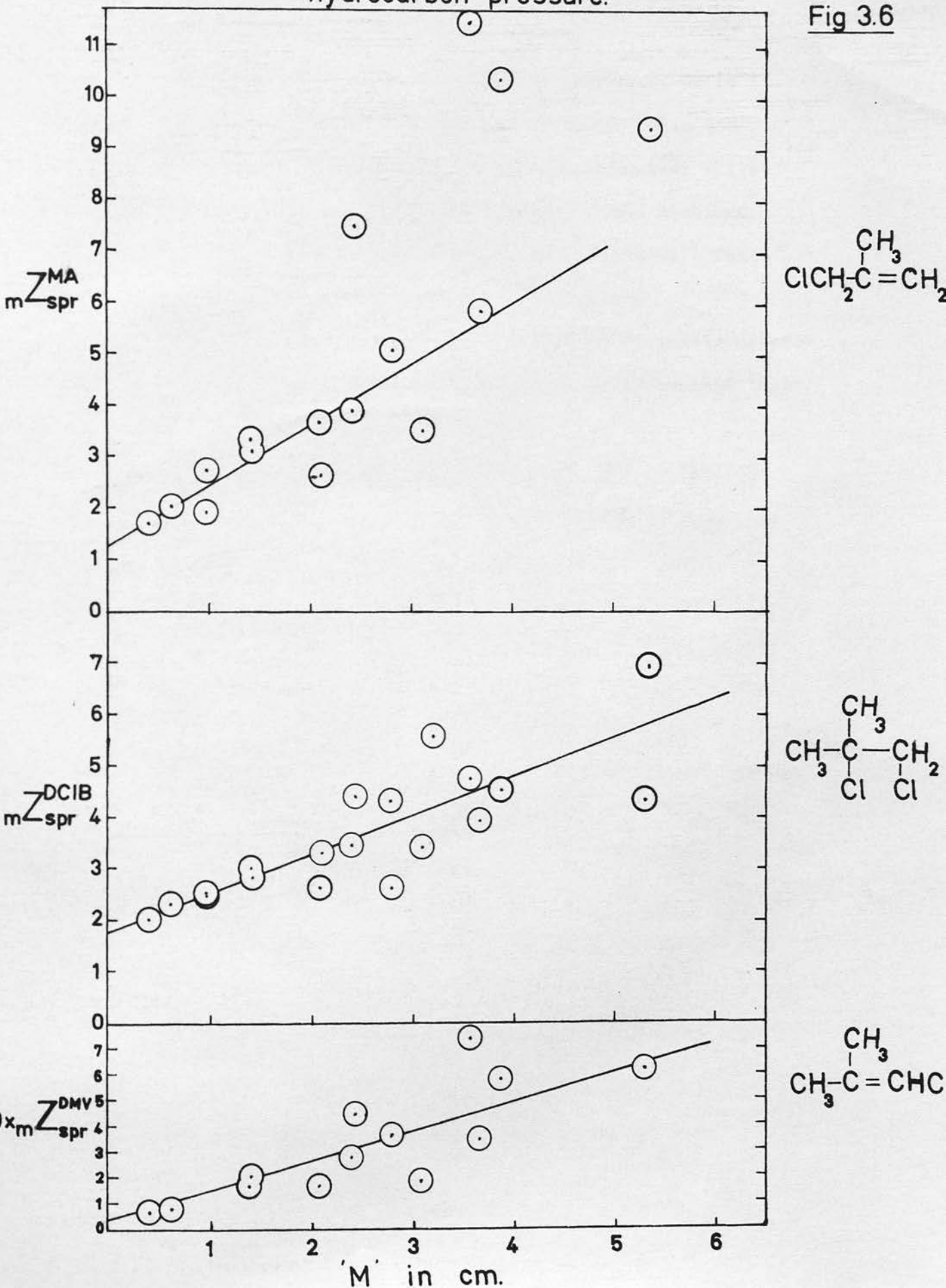
TABLE 3.6

Isobutene/Propane Cl_2 = 1.5 mm. Temp. 35°C

Run	Reactants mm Hg C_4H_8	C_3H_8	Total M	Relative Peak Areas sPrCl	DMV-Cl	M-allyl-Cl	DCIB	$_mZ^{DCIB}_{spr}$	$10X_m$ Z^{DMV}_{spr}	$_mZ^{MA}_{spr}$
B 1a	1.3	29.0	32.1	192	9	96	40	5.60	12.50	13.60
b	2.3	51.3	53.6	182	10	149	51	6.99	13.80	20.60
c	0.4	9.4	9.8	250	Error	26	24	2.54	-	2.74
3b	6.3	17.7	24.0	150	15	209	186	3.48	22.80	3.90
c	10.3	28.6	38.9	94	19	335	146	4.54	5.82	10.40
e	8.1	22.7	31.0	201	13	242	236	3.42	1.87	3.52
f	7.4	20.7	28.0	155	20	270	140	2.65	3.76	5.10
g	9.4	26.3	35.7	100	25	387	162	4.79	7.42	11.50
h	14.1	39.1	53.2	110	24	362	168	4.38	6.25	9.44
i	9.7	27.0	36.7	140	17	283	191	3.98	3.54	5.89
j	3.7	10.4	14.1	189	11	204	185	3.06	1.78	3.36
k	5.6	15.5	21.1	176	None	162	202	3.32	-	2.66
l	3.7	10.5	14.2	194	14	199	179	2.83	2.18	3.13
m	2.5	7.2	9.7	226	Trace	143	182	2.52	-	1.97
n	1.7	4.7	6.4	226	6	149	170	2.35	0.83	2.06
o	1.1	3.1	4.2	225	5	118	142	2.06	0.72	1.71
4f	11.9	12.5	24.4	59	24	402	236	4.41	4.50	7.50
g	13.6	14.2	27.8	46	Error	Error	188	4.36	-	-
h	10.2	10.7	20.9	94	16	317	226	2.64	1.78	3.70
5(20)	18.2	19.8	38.0	None	63	605	111	-	-	-
5(22)	23.4	25.6	49.0	None	60	525	110	-	-	-

Dependence of Z's for Isobutene on total hydrocarbon pressure.

Fig 3.6



3.4 SUMMARY AND INTERIM INTERPRETATIONS.

The three olefine propane systems were found to be complicated and all exhibited pressure dependencies. For the ethylene system the ethylene pressure itself was important whilst for isobutene and propene the rate of formation of the dichloro products depended on the total hydrocarbon concentration. There are two reasonable explanations for these observations.

(1) The chlorination of the olefine may be partly heterogeneous, the heterogeneous reaction having a higher order than that of the free radical homogeneous reaction.

Evidence of a 'dark reaction' was obtained in the isobutene system whilst the propene and ethylene systems were not investigated for this phenomenon. Although no specific tests were applied to show that this 'dark reaction' took place on a surface it is quite apparent from the results that the reaction cannot be entirely bimolecular in nature as at least 8% of the products were formed by hydrogen abstraction. The thermal chlorine atom concentration at 35°C would be extremely small and these abstraction reactions can only reasonably be explained by a process taking place on the wall where chlorine is adsorbed as atomic species.

(2) IF the olefine chlorination is homogeneous a pressure dependence can be explained by supposing the initially formed ·ACl radical is in a vibrationally activated state as proposed by Ayscough et al[39]. Reaction 2 of the simple scheme must then be replaced by the following four reactions

$$A + Cl = \cdot ACl^{*} \qquad 2^{*}$$

$$\cdot ACl^{*} = A + \cdot Cl \qquad (a)$$

$$\cdot ACl^* + Cl_2 = \cdot ACl + Cl_2$$

$$\text{or } ACl_2 + \cdot Cl \qquad (c)$$

$$\cdot ACl^* + M = \cdot ACl + M \qquad (d)$$

where M is a molecule other than chlorine.

Now the rate of formation of ACl_2 will depend on the fraction of $\cdot ACl^*$ radicals which are deactivated before decomposition The normal $\cdot ACl$ radicals are assumed to lead inevitably to the dichloride.

Thus
$$\frac{dACl_2}{dt} = \frac{k_c(Cl_2) + k_d(M)}{k_a + k_c(Cl_2) + k_d(M)} \times \frac{dACl^*}{dt}$$

but
$$\frac{dACl^*/dt}{dC_3H_7Cl/dt} = \frac{k_2^*(A)}{k'_2(C_3H_8)}$$

Therefore
$$\frac{dACl_2}{dt} \Big/ \frac{dC_3H_7Cl}{dt} = \frac{k_2^*(A)}{k_2'(C_3H_8)} \left[\frac{k_c(Cl_2) + kd(M)}{k_a + k_c(Cl_2) + kd(M)} \right]$$

Thus
$$Z \begin{matrix} ACl_2 \\ C_3H_7Cl \end{matrix} = \frac{(ACl_2)(C_3H_8)}{(C_3H_7Cl)(A)} = \frac{k_2^*}{k_2'} \left[\frac{k_c(Cl_2) + k_d(M)}{k_a + k_c(Cl_2) + k_d(M)} \right]$$

It can be seen that provided the relative sizes of k_c and k_d are favourable Z will depend on both (Cl_2) and (M) at low concentrations of each of these reactants; but it will become independent of concentrations at higher pressures when it will yield a true value of k_2^*/k_2'.

The Ethylene system was the only one for which both a hydrocarbon and a chlorine dependence were observed. However as we have seen in 3.1 extrapolation to zero chlorine and zero ethylene pressure gave a value $Z_{spr}^{DCE} = .028$ whereas extrapolation by the above theory gives Z = 0. The intercept value obtained was not large but by reference to figs. 3.1 and 3.2 it can be seen that it

was too large to be accounted for purely by experimental error. Thus whilst the activated radical effect was probably present it was not the only factor effecting this system. A more detailed study of the ethylene system was obviously necessary and was in fact carried out at a later stage. (Chapter 5).

For propylene Miss Thomson found no chlorine dependence and it can be concluded that in this system heterogeneous effects might account for the observations. Consequently the next chapter is mainly devoted to a detailed investigation of surface effects in the propylene system.

The effect of varied chlorine pressure was not studied in the isobutene system, but the reaction proceeded very rapidly and as we have seen there was evidence for at least partial surface catalysis. No further study of the isobutene system was made but it seems likely that the activated radical theory will not be applicable to isobutene or higher olefines for the following reasons. Inherent in the 'activated' scheme is the necessity for deactivation of the excited chloro olefine radical. If deactivation does not occur within a certain time interval the excess energy can become sufficiently localised for the A - Cl bond to break spontaneously. Now the number of vibrational degrees of freedom available in the three olefines studied here, are, 13, 22 and 30 for C_2H_4, C_3H_6 and C_4H_8 respectively. It does not therefore seem unreasonable to expect that at least in the case of isobutene any excess vibrational energy produced by addition of a chlorine atom, would be effectively delocalised by distribution amongst the many available degrees of freedom. Spontaneous decomposition by reaction (a) would not then

occur. Even for propylene the excess energy might be sufficiently dispersed for k_a to be negligible compared to $k_c(Cl_2)$ or $k_d(M)$.

CHAPTER 4.

A Further Study of the Chlorination of Propene : Propane Mixtures.

4.1 INTRODUCTION AND METHOD OF INVESTIGATION

The main purpose of this investigation was to ascertain whether the unexpected dependence of Σ^{DCP}_{spr} on total hydrocarbon pressure, found by Miss Thomson, could be explained in terms of a heterogeneous process. At the same time it was thought desirable to confirm and extend Miss Thomson's observations and to endeavour to find some method for interpretation of the results which would allow the rate constant k_2, for chlorine atom addition to propylene, to be determined.

Preliminary runs carried out with and without photolysis, in a manner analogous to that used for isobutene, showed the presence of a dark reaction. Thus, samples withdrawn from a mixture of propene, propane and chlorine, which had been allowed to stand in the dark for about ten minutes, contained appreciable amounts of 1.2 dichloro propane. However subsequent photolysis of the residual mixture induced the formation of additional products in the form of sec. and p. propyl chlorides and allyl chloride. The fact that these extra products were formed after ten minutes 'dark reaction', whilst in the corresponding case for isobutene no further products were formed on photolysis, implied that the 'dark reaction' was less rapid in the propene system.

Having thus shown the presence of a 'dark reaction' it was next necessary to establish the nature of the process taking place. Whilst it was desirable to study the 'dark reaction' alone, it was felt unlikely that this would be possible for the following reasons.

IF unambiguous results were to be obtained it was essential that the 'reaction zone' be confined to the RV. For this to be possible some method was required by which a reaction could be effectively quenched at any desired stage. Treatment with NOCl, which is commonly used to 'quench' photolytic chlorinations, was not expected to be effective here, where the 'dark reaction' was thought not to be free radical in nature. Though the effect of NOCl was not tested, the above surmise was supported by the fact that in purely photolytic runs carried out in the presence of small quantities of oxygen (which virtually inhibits free radical chlorinations), the production of mono chloro propanes was almost completely inhibited, whilst the 1.2 addition reaction was still considerable. Another method of investigation was therefore required and the procedure adopted was that devised below.

Method of Investigation

It was known that the 'dark reaction' in the chlorination of propene:propane mixtures produced almost entirely 1.2 dichloro propane (with traces of allyl chloride), whilst the photolytic reaction yielded s and p propyl chlorides, allyl chloride, and 1.2 dichloro propane. It was therefore thought that the amounts of mono chloro propanes produced in a reaction carried out with and without photolysis could be used as a measure of the photolytic reaction. At the same time if the reaction was begun in the dark and 'finished-off' by photolysis, all residual chlorine would be consumed and no subsequent reaction could take place outside the RV prior to analysis, These two principles were the basis on which the following scheme was devised.

Experimental

The R.V. was made completely light-free by wrapping a large piece of thick black paper around the heating jacket. The hydrocarbon mixture was then allowed into the darkened R.V.,which already contained the required pressure of chlorine , and the time was noted. After a certain measured time interval the b black paper was removed and the R.V. was exposed to the photolytic light. Photolysis was continued for 15-20 minutes to ensure complete removal of residual chlorine and the products were then analysed.

Interpretation of results.

A complete reaction carried out as above can be depicted schematically as follows:-

	Dark		Light
Cl_2	C_1	C_2	C_3
1.2 $C_3H_6Cl_2$	0	D_2	D_3
s.C_3H_7Cl + p.C_3H_7Cl	0	0	P_3
Time	0	t_d	t_d + 15 minutes

where C=chlorine concentration, D = amount of 1.2 $C_3H_6Cl_2$ produced from propene, P = amount of mono-propyl chlorides from propane, and t_d = time allowed for 'dark' reaction ,ie 'dark time' in minutes.

Assuming the 'dark' reaction is first order in chlorine concentration, we can write -

$$\text{Log}_{10} \frac{C_1}{C_2} = k_d t_d \qquad (1)$$

where k_d is the rate constant for the dark reaction.

Also $$\frac{D_3 - D_2}{P_3} = \bar{K} = \frac{\text{rate of light reaction with olefine}}{\text{rate of light reaction with propane}} \quad (2)$$

Now Initial chlorine = Total chloride products

Thus $$C_1 = D_3 + P_3 \quad (3)$$

and similarly $$C_2 = (D_3 - D_2) + P_3 \quad (4)$$

But from (2) $$D_3 - D_2 = \bar{K} P_3$$

thus substituting in (1) we get

$$\text{Log}_{10} \frac{D_3 + P_3}{\bar{K}P_3 + P_3} = k_d t_d$$

$$\text{or } \text{Log}_{10} \frac{D_3}{P_3} + 1 = k_d t_d + \text{Log}_{10}(\bar{K} + 1)$$

Thus plots of $\text{Log}_{10}(\frac{D_3}{P_3} + 1)$ v t_d should give straight lines of gradient k_d and intercept $\text{Log}_{10}(\bar{K} + 1)$.

The ratio D_3/P_3 = DCP/(nprCl + sprCl) can be easily obtained from the chromatographic analysis.

In practise as the ratio nprCl/sprCl was known to be constant for a photolytic reaction at constant temperature, the ratio D_3/sprCl, was used instead of D_3/P_3.

Let $$D_3/\text{sprCl} = R$$

Then in general

$$\text{Log}_{10}(1 + R) = k_d t_d + \text{Log}_{10}(R_o + 1) \quad (5)$$

where $R_o = \bar{K}$ = the value of R when $t_d = 0$.

Equation (5) was, in fact, found to yield straight line graphs as predicted, and was therefore used throughout the following

investigation.

Note. In deriving equation (5), allyl chloride has been ignored. This is permissable as even under optimum conditions, i.e when $t_d = 0$, allyl chloride usually only amounted to 10% of the total products. Neglection of allyl chloride will not therefore have effected the general overall picture.

4.2 THE EFFECT OF CHANGE OF SURFACE

In this section graphs of $Log(1+R)$ v t_d were obtained for runs carried out in different reaction vessels. The gradients of the lines obtained gave an immediate indication of the rate of the 'dark' reaction. Introduction of 'Hone' valves into the kinetic system at this stage made the changing of reaction vessels a simple operation.

All runs were carried out at 35°C in the manner previously described in 4.1. Reaction mixtures contained 20mm of a nearly one to one mixture of hydrocarbons and 1.5mm of chlorine. For runs at zero 'dark time' the reaction vessel, containing the chlorine, was illuminated just before the hydrocarbon mixture was admitted.

Change in Surface/Volume

The standard procedure for detecting heterogeneity in gas kinetics is to study the effect of an increase in the surface to volume ratio. This investigation was accordingly carried out first.

The reaction in a pyrex vessel of volume 70cc and S/V = $1.8cm^{-1}$ was compared with that in a 100cc vessel whose S/V had been increased to $8cm^{-1}$ by packing with pyrex glass tubes. It can be seen from the results given in Table 4.1 (1a and 1b) and fig. 4.1, that the four-fold increase in S/V produced a ten fold increase in the gradient from $0.01cm^{-1}$ to $0.10cm^{-1}$. Whilst this was more than twice the increase in rate one would expect for a heterogeneous reaction, it seemed certain that wall effects were important in the dark reaction. The difference in the intercepts obtained, implied, that in the packed vessel the surface reaction was sufficiently rapid for it to compete successfully with the photolytic reaction.

Having thus ascertained that a heterogeneous reaction was

present it was thought feasible that a coating might be found for the vessel walls which would render them virtually inert. It would then be possible to study the pure gas phase reaction.

Change of RV surface

Many coatings were tried, some of which had been used before by workers in kinetics (mainly in oxidation work, see later). In the present context for a coating agent to be effective it must:-

(1) Considerably reduce the percentage of wall reaction.

(2) Form a complete coating which would not peel-off, or crack, under vacuum.

(3) Be transparent to the photolytic radiation.

and (4) Be able to withstand heating (for Arrhenius plot)

As will be seen below it was found difficult to obtain all these properties in any one substance.

The following pages are devoted to an account of the different surface coatings used and their method of preparation. They will be dealt with under the headings (a) Clean glass, (b) Carbonaceous films, (c) Inorganic acids, alkalis or salts, and (d) polymeric coatings. The respective graphs are given in figs. 4.3, 4.4, 4.5, and 4.6 and a composite graph is given in fig. 4.7. The analytical results are given in table 4.1.

All the reaction vessels had S/V about $2cm^{-1}$ and were 70cc in volume.

Clean Glass

(1) Pyrex (2) Quartz (3) Soda.

All three vessels were first cleaned with concentrated nitric acid and then washed with distilled water and finally dried.

Quartz and soda glass were equally surface active and more active than pyrex.

All the following RVs were made of pyrex and will be designated by their coatings. As a standard procedure before any runs were carried out in a new vessel it was (a) well pumped down and (b) photolysed twice in the presence of large amounts of chlorine. The latter treatment ensured that any reactive coatings were completely chlorinated.

Carbonaceous Films

(4) Allyl bromide I.

The coating was obtained by pyrolysing a pressure of 15cm of allyl bromide, in the RV, at 330°C for 2 hours. This produced a light brown film of carbonaceous material[99].

(5) Allyl bromide II.

The above RV was treated again this time with 2cm of allyl bromide pyrolysed at 314°C for 10 hours.

(6) Packed RV + Allyl bromide

The pyrex vessel with $S/V = 8cm^{-1}$ was treated by pyrolysing about 10cm of allyl bromide in it at 302° for 17 hours.

The pyrolysing procedures used above produced reasonably even films of carbonaceous material. Allyl bromide I was found to have a reactivity near that of pyrex, but a further coating increased both k_d and the intercept value of Log(1 + R) indicating a catalytic effect. However the second coating was much darker than the first and the enhanced dark rate may have been partly due to a decrease in the intensity of the light penetrating the RV. In the case of the packed vessel where the penetration of the light

must have been limited by the large number of coated glass surfaces, very few products were produced from propane even when t_d was zero. This intercept value was however only slightly higher than that obtained earlier for the packed clean pyrex vessel.

Inorganic Acids, alkalis and salts

(7) Boric Acid I (BAI)

A solution of boric acid in a water and alcohol mixture was sucked into a reaction vessel which had been previously cleaned with nitric acid. This was accomplished by inverting the warmed vessel so that the lead-in tube was in the solution; and then allowing the RV to cool. Alcohol was used to ensure that the mixture wetted the entire surface. An even coating of very fine boric acid crystals was obtained by carefully revolving the vessel whilst evaporating off the solution under suction.

(8) Boric Acid II (BA II Table 4.2 (a)).

This was a similar vessel to the above. Subscripts 2, 3, 4 and 5 in the table of results correspond to four separate attempts to produce a surface of like reactivity to that of Boric acid I. Surfaces 3 and 4 were prepared in an identical way to the above, whilst surface 2 and 5 only differed in the method of final drying. For 2 the RV was gently flamed whilst under suction, whereas for 5 a slow stream of air was led into the vessel centre through a thin tube.

(9) Sodium borate + Boric acid (N.B.B.A)

A procedure similar to $(8)_2$ was used to obtain a thin coating from a solution containing equal quantities of sodium borate and boric acid.

(10) Sodium hydroxide

Procedure as $(8)_2$ using a sodium hydroxide solution. Coating non-uniform.

(11) Potassium chloride

Procedure as $(8)_2$ using a potassium chloride solution.

(12) Phosphoric acid

Two vessels were prepared using 'syrupy' phosphoric acid. (a) was dried by flaming under suction and gave a white somewhat opaque film. (b) was dried by prolonged evacuation while the reaction vessel was warmed in a bath of hot water. In this case a clear film was obtained but the process was extremely lengthy.

All the above coatings except the last were in the form of crystalline deposits and as such, complete coverage of the glass surface was not obtained. It was, for obvious reasons, difficult to obtain a reproducible coating and thus some of the variations in activity observed may have been due to the exposure of more, or less, clean glass surface. The low activity of BAI (which was considerably less active than pyrex glass) could not be reproduced at a later stage when this vessel had unfortunately been cleaned.

Vessel $BAII_5$ was used for some subsequent studies on pressure effects (4.3, 4.4) as results obtained from it were more reproducible than for clean glass.

Whilst the clear phosphoric acid coating certainly gave complete coverage, it apparently catalysed the dichloro-ethane production appreciably.

Polymeric Coatings

Superlose

Superlose is the straight chain fraction of potato starch

(1:4 linked d-glucopyranose). It was used here because it has the property of forming clear adherrent films, but these films were not expected to be very robust under photolytic conditions in the presence of chlorine. The coating was prepared from a solution which was obtained by adding 3% of sodium hydroxide to an aqueous slurry. Evaporation and drying were achieved by pumping only.

Araldite (Ar)

Araldite is an epoxy resin made by CIBA Ltd. The viscous liquid was thoroughly mixed with the required amount of 'hardener' and the mixture was drawn into the RV in the usual way. After allowing the resin to stand at room temperature for 4-5 hours, final hardening was achieved by inverting the RV in a 120° oven for a further 2-3 hours.

It was difficult to make this film uniform, but the interior glass surface was completely covered. A somewhat yellow film was finally obtained.

Poly-vinyl chloride (P.V.C)

Sufficient powdered P.V.C. was dissolved with difficulty in 1.2 dichloroethane. A good transparent colourless film was obtained on removing the solvent under suction. Whilst the film initially gave complete coverage it formed small blisters under high vacuum.

Silcone elastomer (S.E.)

Silicone elastomer dissolved in pet. ether gave a 'gummy' solution which on drying yielded a very good continous and clear coating.

Polythene Fig. 4.2

Small chips of polythene tubing were dropped into a RV previously cleaned with nitric acid. Gentle warming, under reduced

pressure, enabled an almost complete film to be obtained by careful rotation of the reaction vessel. The film was white but semi-translucent.

Urea formaldehyde resin (U.F)

Several different methods and recipes were tried but the following[101] gave the best results.

The reaction vessel was first thoroughly cleaned using nitric acid and alcohol. 5gm of 30% formaldehyde solution were then introduced and heated gently to boiling. A hot aqueous solution of, 1.2gm Urea, 0.022gm monosodium phosphate, 0.08gm disodium phosphate and 0.24gm sucrose, was added dropwise by means of a very narrow-stemmed funnel and the final mixture was evaporated on a water pump until it became cloudy. Clarification was achieved by addition of about 1cc of glacial acetic acid which also accelerated the subsequent drying process. Pumping was continued until the liquid became quite viscous; then by slowly rotating the reaction vessel the clear mixture was made to run over the entire internal surface. The reaction vessel was thereafter inverted, reattached to the water pump, and allowed to drain overnight. Next day it was fixed to the vacuum line and evacuated under high vacuum for 24 hours.

The above treatment yielded a hard transparent and uniform coating which remained unchanged for several months.

(Sucrose was added as a film strengthener[101] as earlier preparations tended to crack easily on drying).

The polymeric coatings in general engendered very much better reproducibility, possibly because more effective surface

covering was obtained.

Although polythene gave the shallowest line, a loss of 1.2 dichloro-propane products became apparent after about 140 minutes dark time and this was thought to be due to solution in the polythene.

Of the others, superlose, silicone, elastomer and araldite, all gave steeper gradients than Urea formaldehyde or P.V.C. These latter two whilst having almost identical gradients gave different intercepts, the P.V.C. intercept being some 0.1 Log units less than that for U.F. The explanation of this is not obvious but as the P.V.C. coating was in general less robust than the urea resin, the U.F vessel was chosen for later experiments.

Change in s/v for U.F. coated Vessel

A packed pyrex vessel of surface to volume ratio 5.8cm^{-1} was coated with U.F resin in the same manner as before. A graphical comparison between the results obtained using this packed vessel, and those for the original vessel whose s/v was 1.8cm^{-1}, can be readily seen in fig. 4.2. Increase in s/v by a factor of 3.2 increased k_d from .007 sec^{-1} to .031 sec^{-1}, a factor of 4.3.

Conclusions:

It is clear from the composite graph (fig. 4.7) that the rate of the dark reaction varied widely with the nature of the surface, but in no case was it reduced to zero. This might have implied the presence of some concurrent homogeneous dark reaction however it is considered that the large rate increases observed on increasing the s/v ratio, virtually rule-out this possibility. These enhanced rates are somewhat curious as, in general, the rate of a heterogeneous process depends on the number of 'active' surface

sites' available for adsorption; thus one would expect that, for a constant pressure of reactants, increase in s/v by a certain factor x, would increase the number of available 'active sites' by a similar factor and the overall reaction rate would therefore be x times as large. If on the other hand, insufficient reactants were present to occupy all the extra 'sites' then the rate would increase by a factor less than x. However in our case, the clean glass surface gave an increased dark rate 2.3 times as large as that expected from the change in s/v, whilst the U.F. vessel gave an increased rate 1.3 times as large as expected. The latter value might be within the experimental error but it seems that the former value at least requires a further explanation. Yuster and Reyerson[19] in their work on the thermal chlorination of propane, noticed that increasing the s/v of their glass reaction vessel, decreased the amount of chlorination taking place. They agreed that this was due to more efficient chain termination on the walls. In our competitive system increased wall termination would decrease the overall rate of both the photo-chemical reactions. However

$$R = \frac{(DCP)_{het.} + (DCP)_{phot.}}{(sprCl)_{phot.}}$$

(where het. and phot. refer to heterogeneous and photochemical formation respectively) thus it can be seen that any increase in R due to an increased heterogeneous rate, will be reinforced by a decrease in the photochemical rate. However for this effect to appreciably alter the gradient (k_d) of the Log(1 + R) v t_d lines wall termination must become proportionally more significant as t_d increaaes. (i.e. $(sprCl)_{phot.}$ must decrease more rapidly than

$(DCP)_{het}$ increases). This is probably true, for, as t_d increases the pressure in the reaction vessel falls, thus wall termination will become progressively more important in the subsequent photolyses.

From the above argument it can be seen that the urea formaldehyde surface is not only relatively inert for the heterogeneous chlorination of propene but, as one might therefore expect, it is also much less effective than glass as a termination of reaction chains.

The packed reaction vessels produced Log(1-R) v t_d graphs which levelled off after a certain time indicating that some propyl chlorides had been formed in the dark. It can be seen from the tables that the amount of sec propyl chloride formed in these circumstances was small and similar to that obtained from unpacked vessels in which reactions mixtures were left overnight before photolysis. e.g. PI, $BA(9)_5$, PVC12. It is not thought likely that any light leaked into the reaction vessel thus a very small amount of heterogeneous chlorination of propane seems to be the best explanation of this phenomenen. The levelling-off must correspond with the complete removal of chlorine and would thus be expected to be observed earlier in those systems where the surface was particularly active. It was in fact observed in the unpacked KCl vessel which was the most reactive surface studied. For the less reactive surfaces td was not usually extended sufficiently to observe this levelling-off effect.

The study of surface effects in gas kinetics has mainly been confined to those occurring in hydrogen or hydrocarbon oxidation

systems. Thus a KCl coated vessel has been found to reduce the rate of methane oxidation [102] at 500° and is an effective inhibitor of the slow oxidation of hydrogen between the second and third explosion limits[103]. Boric oxide coated, or HF treated silica vessels[103] on the other hand, gave very fast rates of oxidation for both these reactions. Retardation was thought to be due to heterogeneous destruction of HO_2 and/or H_2O_2.

A parallel effect of change in surface was observed in our system where KCl gave results consistent with a very large amount of heterogeneous chlorination, whilst a boric acid coating was relatively inert. The uncoated glass vessels used here were only cleaned using concentrated nitric acid (not HF) and the resulting activity was intermediate between those of KCl and boric acid. Phosphoric acid in contrast to boric acid had a reactivity greater than that of clean quartz glass.

TABLE 4.1

(Reactants:- Cl_2 = 1.5mm, C_3H_6 = 9.5mm, C_3H_8 = 10.5mm)

(1)a Pyrex s/v = $1.8cm^{-1}$

Run	sprCl	Allyl-Cl + nprCl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1 + R)$	t_d
P1	1.2	Error	162.0	121.00	2.086	5400
3	50.0	65.6	92.2	1.84	0.453	5
5	38.8	47.4	96.8	2.49	0.543	13
6	14.5	20.8	163.0	11.25	1.088	70
9	5.1	10.7	171.0	33.50	1.538	118
10	24.7	33.8	147.0	5.95	0.842	61
11	56.7	Error	88.4	1.56	0.408	0

(1)b Packed Pyrex s/v = $8.0cm^{-1}$

PRV 2	0.3	12.7	316	1055	3.024	15
3	2.6	15.4	291	112	2.053	0
4	0.3	13.8	335	1118	3.049	32
5	0.5	14.3	317	634	2.803	10
6	0.45	10.9	268	596	2.776	5

(2) Quartz s/v = $1.8cm^{-1}$

Q 2	20.0	30.6	170	8.5	0.978	23
3	0.6	Error	162	270.0	2.433	115
4	2.2	10.0	182	82.7	1.923	82
5	42.4	58.4	130	3.06	0.609	11
6	0.6	7.4	175	292.0	2.467	139

(2) Quartz s/v = 1.8cm^{-1} (contd.)

Run	sprCl	Allyl Cl + nprCl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1 + R)$	td
Q 7	15.0	23.8	164	10.9	1.076	42
8	6.0	14.1	174	29.0	1.477	64
9	12.4	15.7	16.6	1.34	0.369	0

(3) Soda

S 2	18.0	32.6	211	11.71	1.104	40
3	7.5	20.3	245	32.62	1.527	99
4	50	Error	149	2.98	0.600	11
5	4.9	7.3	32.1	6.55	0.878	6
6	0.4	7.8	225.1	563.0	2.751	136
7	12.0	17.3	22.0	1.83	0.452	0

(4) Allyl Bromide I

AB 9	39.3		176	4.48	0.739	30
10	4.5	10.8	158	35.1	1.558	126
11	34.2		116	3.39	0.643	15
12	38.0		108	2.84	0.584	20
13	33.4	46.9	117	3.50	0.653	25
14	37.1	50.9	106	2.86	0.587	10
15	46.1		96.6	2.09	0.490	5
16	48.2		95	1.98	0.474	0

(5) Allyl Bromide II

AB 20	31.5	44.4	150	4.76	0.760	0
22	1.3	7.4	183	141	2.152	52

(5) Allyl Bromide II (Contd.)

Run	sprCl	Allyl Cl + nprCl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1 + R)$	td
AB 23	7.4	14.4	197	26.6	1.441	32
24	30.0	43.4	149	4.96	0.775	0
25	21.0	30.3	139	6.64	0.883	10
			(6) Packed + Allyl Bromide s/v = $8.0cm^{-1}$			
PAB 2	None	1.7	250	-	-	35
3	0.3	2.6	78	260	2.416	0
			(7) Boric Acid I			
$BA(3)_1$	49.7	62	88.5	1.78	0.440	6
$(4)_1$	34.0	45.5	116.0	3.41	0.644	37
$(5)_1$	20.0	29.6	148.0	7.4	0.924	79
$(6)_1$	54.7	Error	70.6	1.29	0.360	1
			(8) Boric Acid II see Table 4.2 (a)			
$(25)_5$	6.2	16.9	135	21.8	1.358	70
$(27)_5$	33.5	51.5	92	2.74	.573	5
$(28)_5$	15.3	27.3	119.5	7.82	.946	35
			(9) Sodium Borate + Boric Acid			
NBBA2	.3	1.56	28.4	94.7	1.981	118
3	9.7	13.9	15.7	1.62	.418	0
4	4.1	6.6	22.9	5.58	.818	28
			(10) Sodium Hydroxide			
NaOH 1	4.0	6.9	21.6	5.40	.806	0
3	1.0	2.7	35.6	35.6	1.564	26
4	0.3	-	31.4	104.7	2.024	62

(11) Potassium Chloride

Run	sprCl	Allyl Cl + nprCl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1 + R)$	td
KCl 3	22.5	36.2	139	6.18	.856	0
5	1.2	7.4	149	124	2.097	28
7	0.2	4.9	150	750	2.876	98

(12) Phosphoric Acid

PA 1	8.8	11.4	15.3	1.75	.439	0
2	0.8	1.3	18.0	22.5	1.371	40
3	9.5	13.9	13.3	1.40	.380	0

(13) Superlose

SU 1	11.2	13.4	15.7	1.40	.380	0
2	2.0	3.6	28.4	14.2	1.182	69
3	6.9	9.9	19.4	2.82	.582	16
4	4.2	6.5	25.9	6.16	.855	25
5	10.9	14.3	17.0	1.56	.408	0
7	0.4	7.9	168	420	2.624	246

(14) Araldite

AR 1	5.9	9.1	9.3	1.58	.412	0
2	9.0	12.0	15.7	1.75	.439	16
3	0.7	2.7	25.2	36.0	1.568	159
4	1.8	3.6	18.4	10.2	1.049	118

(15) Poly-Vinyl Chloride

PVC 1	8.7	9.3	23.6	2.71	.569	43
2	15.7	18.5	16.2	1.03	.308	0
5	15.5	20.2	150	9.68	1.029	122
9	48.5	64	94.6	1.95	.470	29
10	15	19.1	14.9	.994	.300	0

(15) Poly-Vinyl Chloride (Contd.)

Run		sprCl	Allyl Cl + npr Cl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1+R)$	td
PVC	11	12.8	16.7	17.4	1.35	.371	12
	12	0.2	Error	22.7	113.5	2.059	950
	13	9.3	16.1	152	16.36	1.239	134
	15	6.3	8.45	29.4	4.66	.753	82
			(16) Silicone Elastomer				
SE	2	3.2	2.7	91	2.84	.584	25
	3	3.9	4.8	1.25	1.09	.318	0
	4	0.6	1.3	15.2	25.3	1.420	102
			(17) Polythene				
P	1	16.9	24.8	57.4	3.39	.643	38
	2	13.3	17.9	60.0	4.51	.741	66
	3	33.4	28.1	68.0	2.03	.480	15
	4	3.4	2.6	42.5	12.5	1.130	175
	5	39.5	57.4	56.8	1.44	.387	0
	6	4.4	8.3	51.2	11.6	1.100	120
	7	9.4	13.7	28.0	2.98	.600	29
	8	20.2	27.2	27.8	1.38	.377	5
	9	3.1	5.45	21.7	7.0	.903	222
			(18)a Urea formaldehyde s/v = $1.8cm^{-1}$				
			(Reactants:- Cl_2 = 3mm, C_3H_8 = 8.6mm, C_3H_6 = 9.9mm)				
UF	1	13.4	18.8	44.8	3.34	0.638	32
	2	6.8	10.3	59.5	8.75	0.989	82
	3	17.9	25.1	35.7	1.99	.476	10
	4	0.6	3.0	73.9	123	2.093	230

(18)a Urea formaldehyde s/v = $1.8cm^{-1}$ (contd.)

Run	SprCl	Allyl Cl + nprCl	DCP	$\frac{DCP}{sprCl} = R$	$Log_{10}(1+R)$	td
UF 5	20.9	29.2	29.2	1.40	.380	0
6	15.2	21.4	47	3.1	.613	31
7	9.2	24.4	235	25.6	1.425	160
8	10.5	15.2	41.5	3.95	.695	45.5

(18)b Packed Urea formaldehyde s/v = $5.8cm^{-1}$

PUF 1	10.1	16.4	30.7	3.04	.606	0
2	1.45	17.8	175	121	2.086	125
3	.2	3.25	41	20.5	1.332	24
4	8.2	13.1	39	4.75	,760	5
5	7.2	12.2	40.5	5.6	.820	6
6	2.7	21.4	224	83	1.924	118
7	2.4	20.7	226	94	1.978	139
8	0.7	4.8	49.4	70.6	1.855	63
9	5.8	24.9	240	41.4	1.627	33
10	11.9	32.1	268	22.5	1.371	21

Effect of different surface conditions on Propene system. Log(1+R) v t_d graphs.

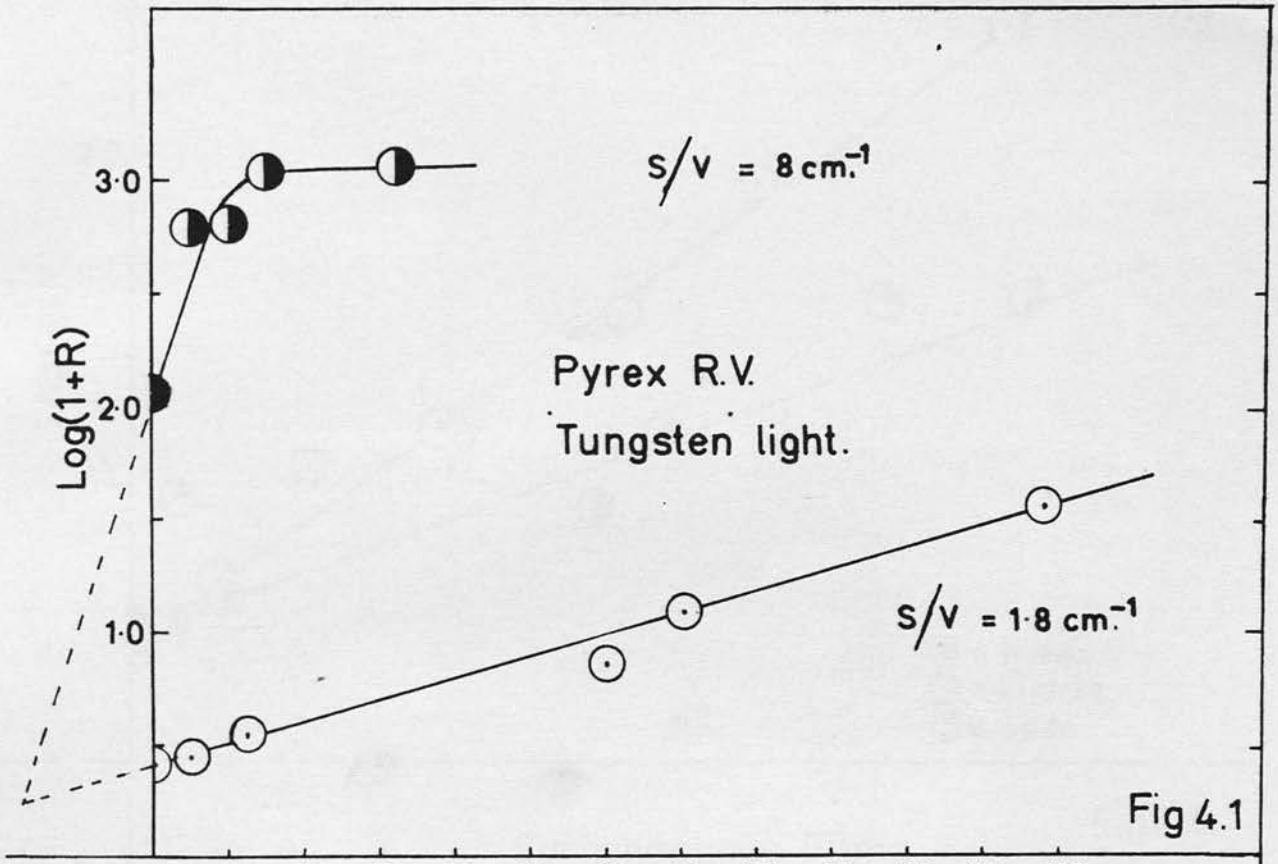


Fig 4.1

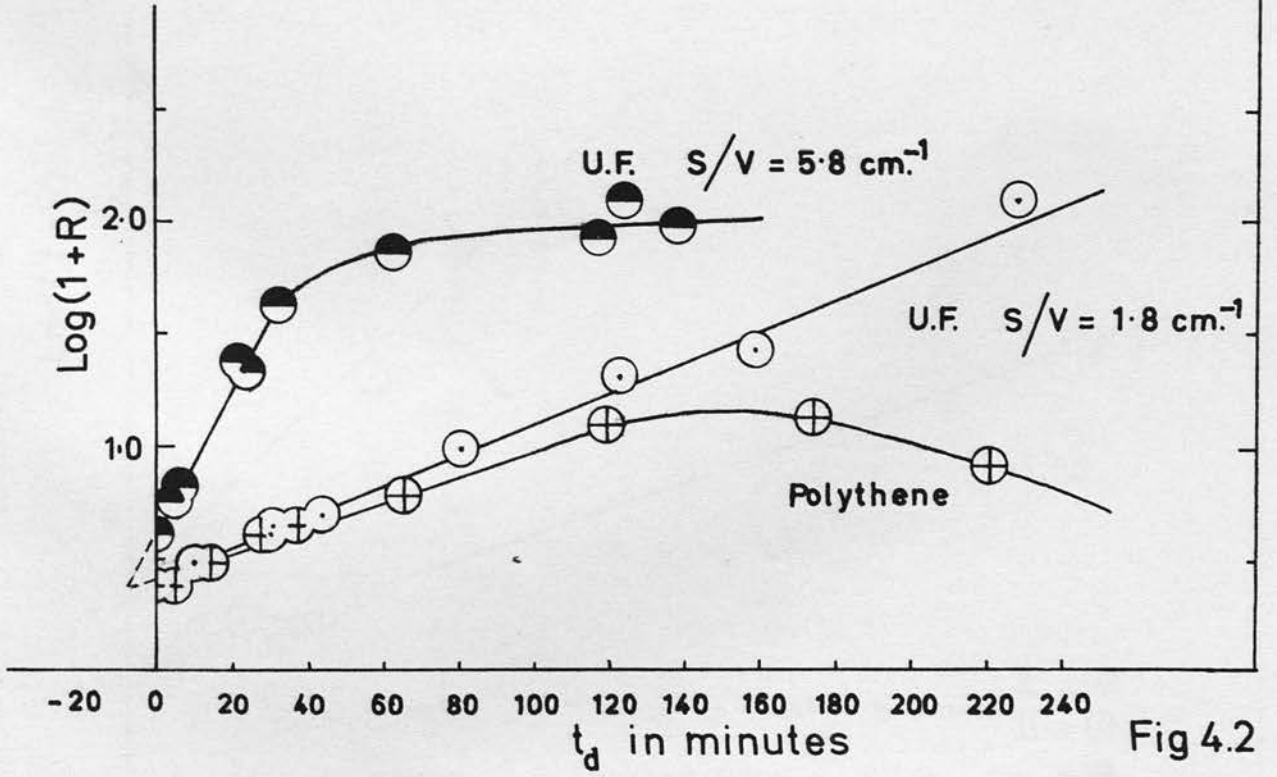


Fig 4.2

Clean Glass Surfaces

Fig 4.3

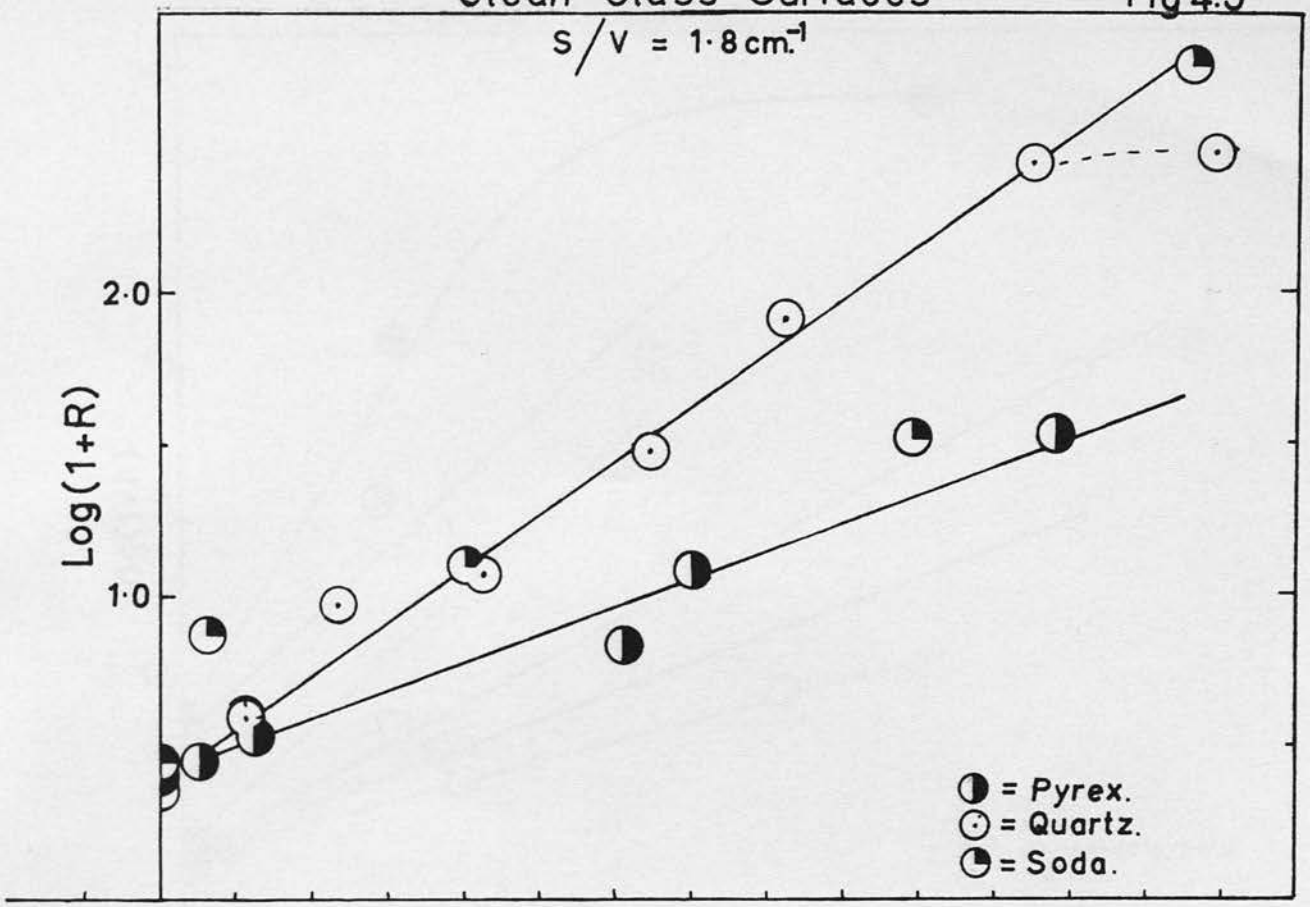


Fig 4.4

Carbonaceous Films

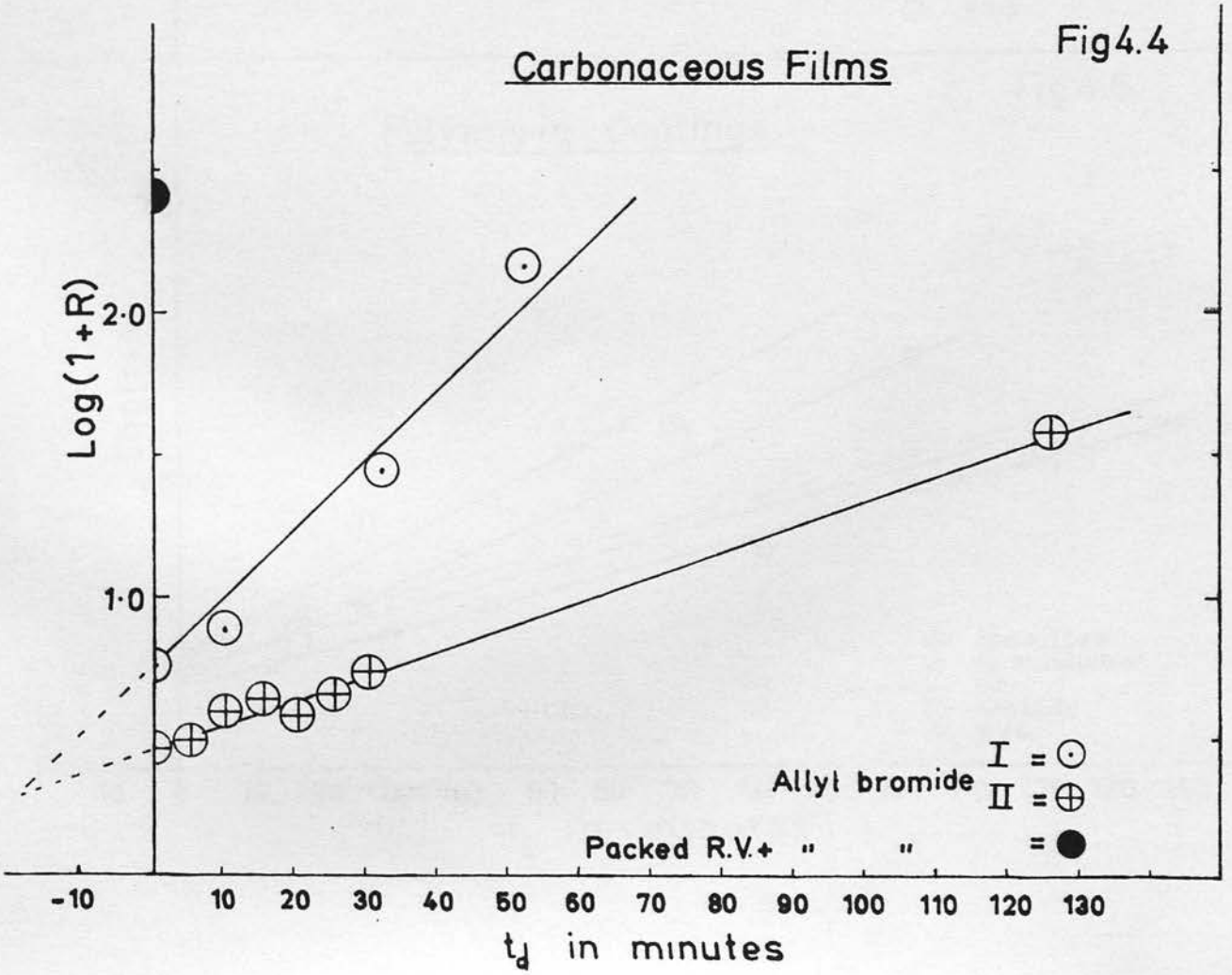


Fig 4.5

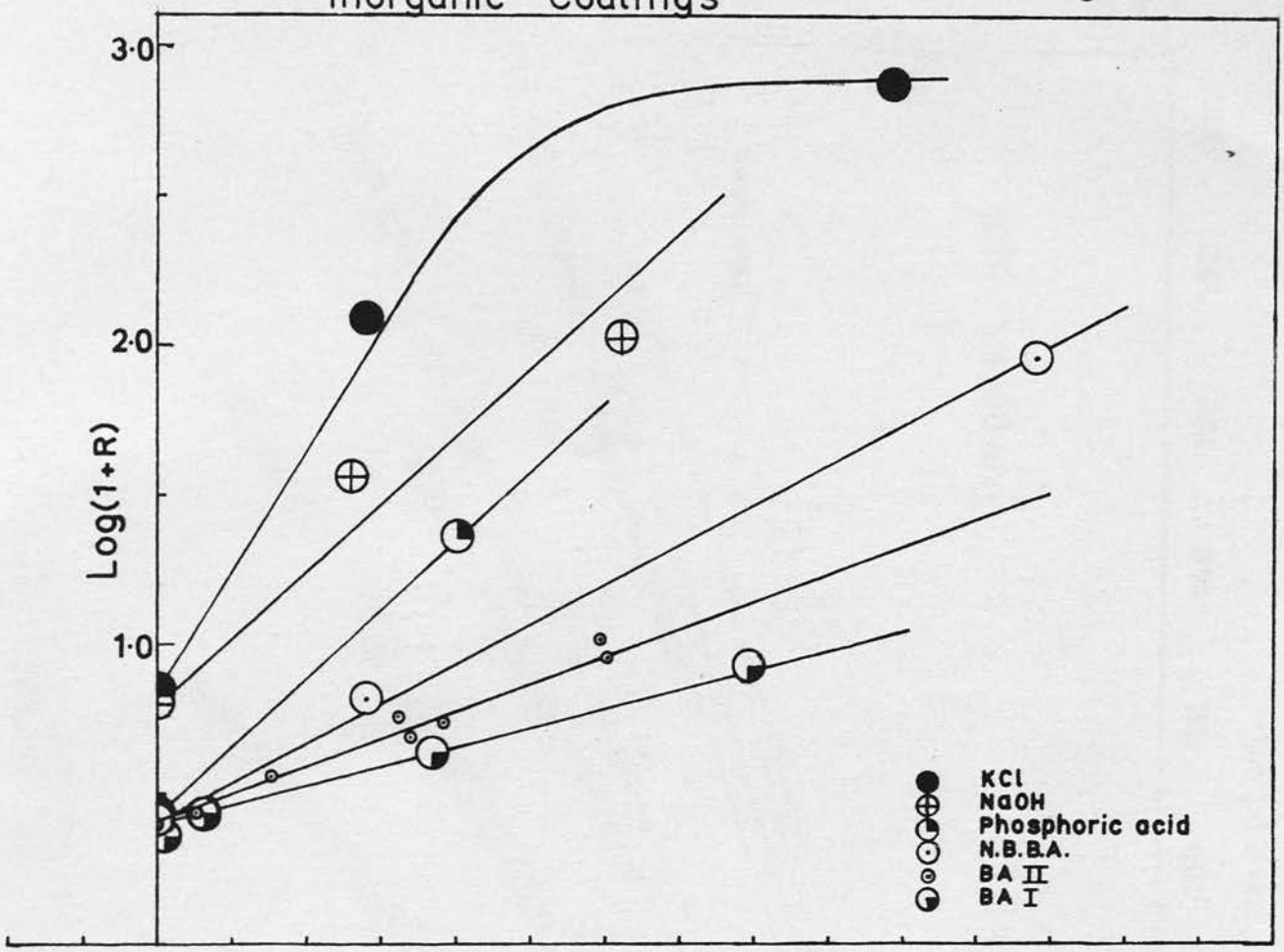
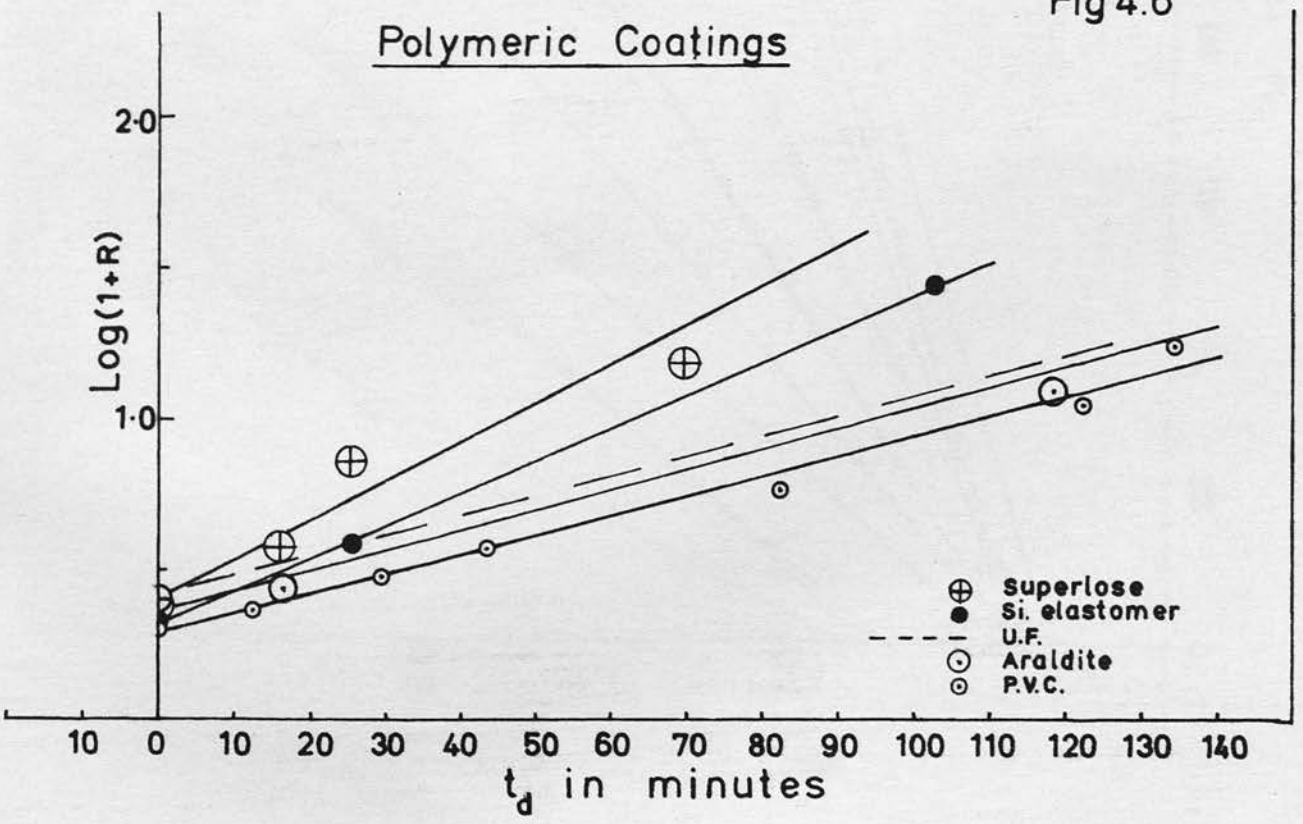

Inorganic Coatings
3·0
2·0
1·0
Log(1+R)
KCl
NaOH
Phosphoric acid
N.B.B.A.
BA II
BA I

Fig 4.6


Polymeric Coatings
2·0
1·0
Log(1+R)
Superlose
Si. elastomer
U.F.
Araldite
P.V.C.
10 0 10 20 30 40 50 60 70 80 90 100 110 120 130 140
t_d in minutes

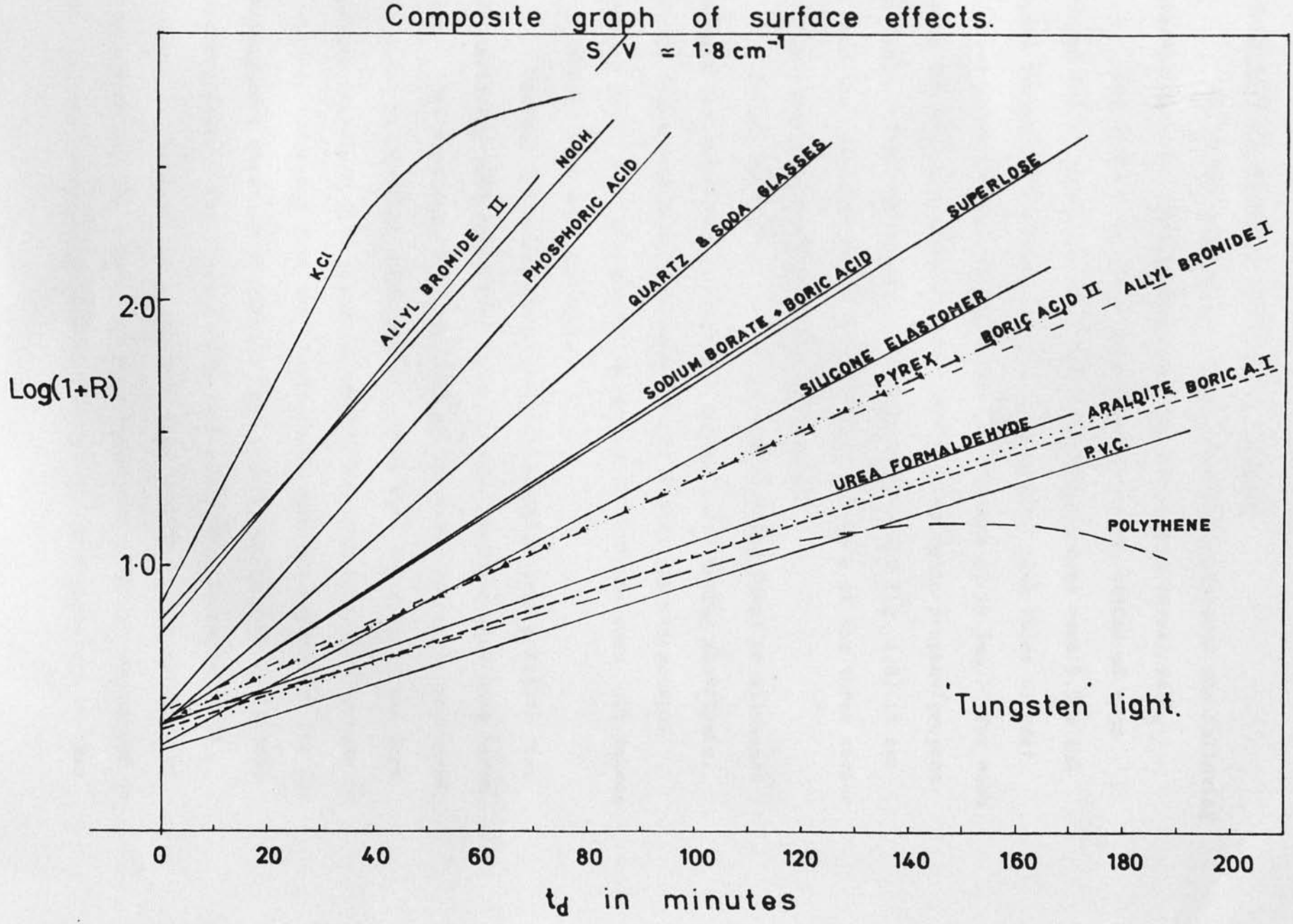

Composite graph of surface effects.
S/V ≈ 1·8 cm⁻¹
KCl
ALLYL BROMIDE II
NaOH
PHOSPHORIC ACID
QUARTZ & SODA GLASSES
SODIUM BORATE + BORIC ACID
SUPERLOSE
SILICONE ELASTOMER
PYREX
BORIC ACID II
ALLYL BROMIDE I
UREA FORMALDEHYDE
ARALDITE BORIC A.I
P.V.C.
POLYTHENE
'Tungsten' light.
Log(1+R)
2·0
1·0
0
20
40
60
80
100
120
140
160
180
200
t_d in minutes

Fig 4.7

4.3 EFFECT OF CHANGE IN HYDROCARBON PRESSURE

While the polymeric coatings were being prepared the following investigation was carried out using the boric acid vessel $BAII_5$.

Log (1+R) v t_d plots wereobtained for two series of runs (b) and (c) in which the total hydrocarbon pressures were 9.5mm and 34.2mm respectively, these results were coupled with those already reported above for (a) at a hydrocarbon pressure of 19.5mm. For each series the chlorine pressure was 1.5mm and the ratio propane/propene was 0.88. From the results and graphs (Table 4.2 fig. 4.8) it can be seen that straight lines were obtained for each of the three series and that they intersect at about -18 minutes.

In our derivation of the equation for Log (1+R) no allowance was made for heterogeneous reaction taking place during photolysis. Had the light source been of such intensity that the homogeneous reaction could be considered to be virtually instantaneous, all values of R_o should have been the same.

However the homogeneous reaction actually took a finite time and inevitably some concurrent heterogeneous reaction must have taken place. The fact that the gradients of the lines obtained, increased with total hydrocarbon pressure, indicates that the rate of the dark reaction increased with pressure, whilst the corresponding increase in R_o values, indicates that this increase in rate was sufficient for the heterogeneous reaction to compete more significantly with the photolytic reaction. The lines in fig. 4.8 would thus be expected to intersect as observed, at a negative time similar to the duration of illumination and the R value of this intersection should correspond to 100% homogeneous reaction (see section 46 for interpretation on this

basis)

As the intercepts R_o increase with pressure the corresponding values of Z_{spr}^{DCP} must also increase with pressure and this was exactly what Miss Thomson found in the preliminary investigation. We have further confirmed her results in section 4.5.

TABLE 4.2

Effect of Change in Hydrocarbon Pressure

(Reactants:- Cl_2 = 1.5mm (a) C_3H_8 = 9.5mm C_3H_6 = 10.5mm)

Run	sprCl	Allyl Cl *nprCl	DCP	R	$Log_{10}(1+R)$	t_d
BA $(1)_2$	10.1	14.3	13.3	1.32	0.366	0
$(2)_2$	10.1	14.2	13.7	1.35	0.371	0
$(3)_2$	14.6	25.6	138	9.45	1.019	59
$(1)_3$	9.2	13.3	13.3	1.45	0.389	0
$(2)_4$	0.2	1.59	27.8	139.0	2.146	216
$(3)_4$	0.5	-	27.0	54.0	0.740	38
$(1)_5$	9.1	13.1	12.8	1.41	0.382	0
$(2)_5$	0.8	-	18.8	23.5	1.389	111
$(5)_5$	16.1	27.3	128.6	7.98	0.953	60
$(6)_5$	34.5	49.6	91.6	2.70	0.568	5
$(7)_5$	8.8	12.2	14.9	1.69	0.430	5
$(8)_5$	5.1	8.2	19.8	3.88	0.688	33.5
$(9)_5$	0.1	1.3	29.8	298.0	2.476	960
$(10)_5$	23.1	36.2	109.5	4.74	0.759	32

(b)

(Reactants:- Cl_2 = 1.5mm, C_3H_8 = 4.44mm, C_3H_6 = 5.06mm)

BA $(15)_5$	9.1	17.3	127	13.9	1.17	118
$(16)_5$	39.8	54.6	73.5	1.85	.455	13
$(17)_5$	5.4	7.6	19.5	3.61	.664	48
$(18)_5$	10.0	13.1	12.5	1.25	.352	0
$(20)_5$	36.3	50.9	83	2.28	.516	26
$(23)_5$	47.1	Error	59.3	1.26	.354	0
$(26)_5$	15.1	24.4	126.5	8.38	.972	94

(c)

(Reactants:- Cl_2 = 1.5mm, C_3H_8 = 1.60, C_3H_6 = 1.83)

$BA(11)_5$	21.4	32.1	106	4.96	.775	18
$(12)_5$	7.5	10.9	15.3	2.04	.483	0
$(13)_5$	5.1	15.2	138.8	27.2	1.435	83
$(14)_5$	6.3	15.7	130	20.6	1.314	58
$(24)_5$	22.1	36.6	109.5	4.95	.775	18

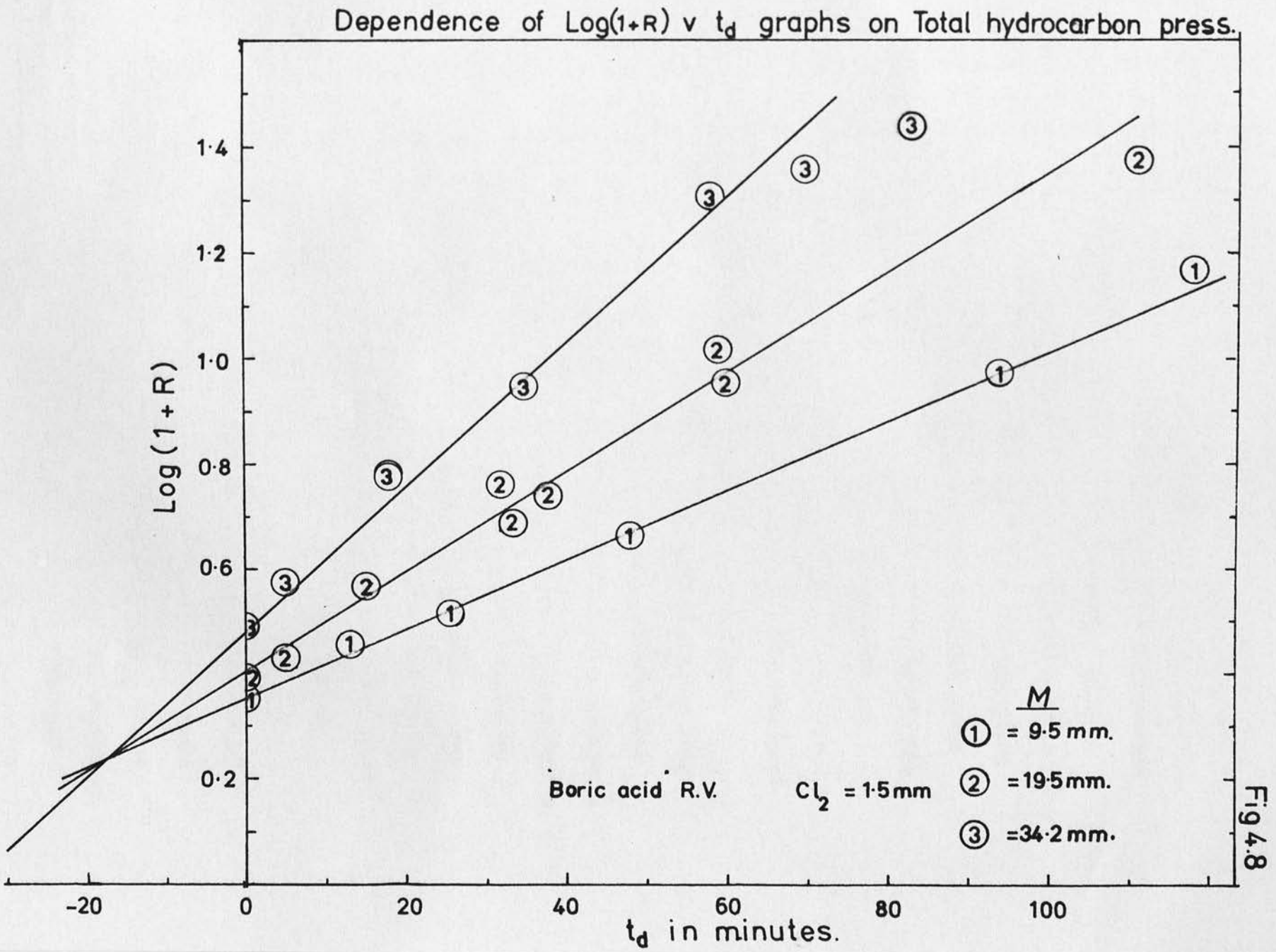

Dependence of Log(1+R) v t_d graphs on Total hydrocarbon press.
Log (1 + R)
1·4
1·2
1·0
0·8
0·6
0·2
-20
0
20
40
60
80
100
t_d in minutes.
Boric acid R.V.
Cl_2 = 1·5mm
M
① = 9·5 mm.
② = 19·5 mm.
③ = 34·2 mm.

Fig 4.8

4.4 THE EFFECT OF CHANGE IN CHLORINE PRESSURE

The dependence of iZ^{DCP}_{spr} on chlorine pressure for hydrocarbon mixtures of 34.2cm, was studied in the boric acid vessel, $BAII_5$. As in Miss Thomson's work in an uncoated pyrex vessel, the concentration ratio was found to be constant for chlorine pressures between 1.5mm and 5mm Hg (fig. 4.9). The constant value obtained here was lower than that obtained by Miss Thomson, but this fact is consistent with the difference in hydrocarbon pressures used in the separate investigations.

At pressures of chlorine below 1.5mm the Z^{DCP}_{spr} ratio was found to be no longer independent of chlorine pressure but increased rapidly as the pressure decreased (Miss Thomson carried out two runs below 1.5mm but her results do not concur with those obtained here. However, she used a mercury manometer to measure the chlorine pressures and the mercury surface was consequently covered with mercuric chloride which almost certainly made small pressure measurements inaccurate). The overall chlorine dependence graph was hyperbolic in shape, thus Z^{DCP}_{spr} is proportional to $1/(Cl_2)$. Two possible explanations can be suggested for this inverse dependence on chlorine pressure, but first it is necessary to deal briefly with the mechanism of the surface reaction.

In accordance with the postulate first made by H.S. Taylor[104] the surface reaction can be considered to take place only on a number of specially favoured 'sites'. These so called active sites differ for each reactant but the whole surface may be available for adsorption of reactant or product molecules thus the majority of adsorbed gas may be held on non-active sites. In the system under discussion it

is assumed that reaction takes place between adsorbed chlorine and adsorbed propene held on their respective 'active sites'. Both of the following explanations for shape of the chlorine dependence graph, involve the basic idea that as the chlorine pressure falls below a certain level, the rate of the surface reaction, increases whilst the relative ratesof the photolytic reactions remain constant.

(1) If chlorine is strongly adsorbed and can occupy certain of the 'active sites' for propene then increase in chlorine pressure will reduce the rate of reaction in a hyperbolic manner, the limiting value being reached when chlorine occupies a maximum number of the active propene sites. The reaction will then be zero order with respect to chlorine. If the chlorine pressure is reduced below the limiting pressure the reaction rate will progressively increase until the chlorine occupies none of the active sites for propene.

(2) If a reaction product can be strongly adsorbed on some of the active reactant sites than a limited 'poisoning' of the surface will take place similar to that in (1). Thus if less chlorine is initially present than is required to saturate these active sites with product, the overall reaction will be activated. This activation will be apparent until the chlorine pressure is increased to a level where the amount of reaction required to deactivate the surface is only a very small percentage of the total reaction.

Now although both (1) and (2) will account for the observed chlorine dependence, the characteristics of the <u>dark reaction</u> will be different for the two cases. Thus for (1) a dark reaction; carried out at a pressure of chlorine above the limiting value,

would be expected to proceed at a steady rate until the chlorine pressure fell sufficiently for the extra active sites for propene to be exposed. The dark rate should then increase progressively as more and more of the originally chlorine 'poisoned' sites, became available for the propene. On the other hand for (2) the same study would be expected to show an initial burst of reaction followed by a steady rate which would continue till all the chlorine was consumed. It might therefore be expected that one or other of these phenomena would be observed in the Log(1+R) v t_d graphs. The fact that neither initial nor final 'bursts' of reaction were actually observed in this system does not necessarily mean that neither effect was present, for whilst (1) should certainly have been observed, especially in those cases where almost total consumption of chlorine took place in the dark, the process outlined in (2) could have been virtually instantaneous at the chlorine pressures used here, in which case the graphs would not curve upwards at low values of t_d. (There is some evidence that (2) does in fact occur in the ethylene system. See chapter 5).

Up to this point chlorine pressures of 1.5mm or 2mm had been used for the various investigations. However as these pressures were near the point of curvature in the chlorine dependence graph, it was decided to use slightly higher chlorine pressures for subsequent work on this system.

4.5 THE EFFECT OF CHANGE IN LIGHT INTENSITY

From the foregoing investigations it appeared that the rate of the surface reaction in the propene system, was sufficiently large for it to compete with the photolytic reaction. It was realised that the significance of this competition should be decreased if the light intensity and hence the rate of the photolytic reaction were increased. Accordingly the light source was changed from the original tungsten lamp to a 300 watt mercury vapour lamp.

Plots of iZ^{DCP}_{spr} v hydrocarbon pressure are shown in fig. 4.10 for both the tungsten and mercury lights. The urea formaldehyde coated vessel was used and the chlorine pressure was kept at 3mm.

The line obtained here for the tungsten lamp was slightly steeper than that obtained by Miss Thomson on clean glass (the gradient here was $0.27cm^{-1}$, whereas Miss Thomson obtained $0.20cm^{-1}$), whilst the intercept was somewhat lower (0.72 here, cf 0.85 for Miss Thomson). The increased intensity of the UV lamp on the other hand reduced the gradient to 0.136 whilst the intercept value was virtually unchanged, Thus increased light intensity decreased the pressure dependence, as expected and this can be taken as further evidence that the dependence on total hydrocarbon pressure was due to the surface reaction and not to an activated radical effect. However whilst a linear dependence on propene pressure is what one would expect for a surface reaction where propene was only slightly adsorbed, it is not at all clear why the pressure of propane should also be important. Propane might in some way act as a 'promoter' of the surface reaction, or perhaps a small amount of homogeneous bimolecular dark reaction takes place between chlorine and propene, and the remaining hydrocarbons serve

as inert gas and help to conduct excess heat to the walls. Unfortunately the effect of inert gas was not tested in this system.

A graph of iZ_{spr}^{allyl} is also given in fig. 4.10. These results are for the UV photolysis and while they concur with Miss Thomson's results in being virtually independent of hydrocarbon pressure, the intercept value is some 20% lower than she obtained.

Note: In all the work in this chapter peak heights were used as a means of evaluating peak areas. This decreased the time required per experiment, and hence increased the number of experiments that could be carried out. The calibration factors required to convert heights to areas were determined by planimetering several runs chosen at random. In order to obtain reproducible results by this method the column temperature was kept constant (at 60°) throughout the analyses.

As pointed out earlier the chromatography column used for this work did not separate the n propyl chloride and allyl chloride products; in fact one composite peak was obtained. The values for allyl chloride, sued for the graph in fig. 4.10 were obtained by first calculating the area of the n propyl part of the composite peak (using the known value for sec. propyl chloride, and the ratio spr/ppr = 1.20) and then subtracting this from the total area of the composite peak.

TABLE 4.3

Dependence of iZ^{DCP}_{spr} on chlorine pressure. (Boric acid Vessel)

(Reactant pressures:- C_3H_6 = 18.2mm, C_3H_8 = 16.0mm)

Run	Cl_2 in mm Hg	Relative Peak Areas			iZ^{DCP}_{spr}
		sPrCl	Allyl Cl + nPrCl	$C_3H_6Cl_2$	
Cl 1	4.5	25.6	35.4	46.0	1.59
2	0.5	8.9	14.8	22.8	2.24
4	4.5	24.7	35.1	46.8	1.66
5	1.0	23.6	36.0	56.0	2.06
6	3.0	16.3	24.3	31.9	1.72
7	0.25	4.5	-	168.0	3.26
8	2.5	12.3	-	24.4	1.73
9	0.25	2.6	4.16	11.2	3.76
10	1.5	7.5	10.9	15.3	1.78

Dependence of iZ^{DCP}_{spr} on hydrocarbon pressure (UF vessel)

(Reactants Cl_2 = 3mm, $\frac{\text{Propane}}{\text{propene}}$ = 0.935, Tungsten Light)

Run	Mixture pressure in mm	Relative Peak Areas			iZ^{DCP}_{spr}
		sPrCl	Allyl Cl + nPrCl	$C_3H_6Cl_2$	
UF 9	18.2	20.9	29.2	29.2	1.23
10	18.5	21.3	30.5	36.5	1.48
11	17.3	19.7	27.0	24.9	1.10
12	11.7	20.0	26.8	21.2	0.93
13	10.0	21.1	28.4	24.9	1.03
14	9.0	21.8	28.7	22.4	0.90
15	5.9	20.4	27.2	18.5	0.80
16	1.97	22.0	31.2	30.5	1.30

Run	Mixture pressure in mm	Relative Peak Areas sPrCl	Allyl Cl + nPrCl	$C_3H_6Cl_2$	iZ^{DCP}_{spr}
17	29.5	19.2	26.8	29.0	1.41
18	34.7	17.2	24.0	31.1	1.69
19	45.7	14.3	21.6	34.8	2.27
20	17.3	19.0	25.1	25.7	1.26
21	52.0	14.8	21.7	31.1	1.96
22	31.5	17.3	24.4	26.6	1.44

Mercury Vapour Lamp

Run	Mixture pressure in mm	sPrCl	Allyl Cl + nPrCl	nPrCl calculated	Allyl Cl calculated	$C_3H_6Cl_2$	iZ^{DCP}_{spr}	iZ^{Allyl}_{spr}
UV1	19.6	19.7	23.7	16.4	7.3	20.8	0.99	0.35
2	19.6	19.4	24.2	16.2	8.0	22.1	1.07	0.39
3	17.2	19.1	24.3	15.9	8.4	19.2	0.95	0.41
4	26.8	17.5	22,6	14.6	8.0	20.2	1.08	0.44
5	34.6	17.0	22.3	14.2	8.1	21.0	1.15	0.45
6	46.7	17.7	23.4	14.7	8.7	25.6	1.36	0.46
7	11.1	23.3	28.0	19.4	8.6	22.1	0.89	0.35
8	50.5	57.0	76.6	47.5	29.1	90.0	1.48	0.48
9	6.3	62.0	81.0	51.5	29.5	55.0	0.83	0.44
10	68.1	50.0	-	-	-	87.0	1.63	-

Fig 4.9

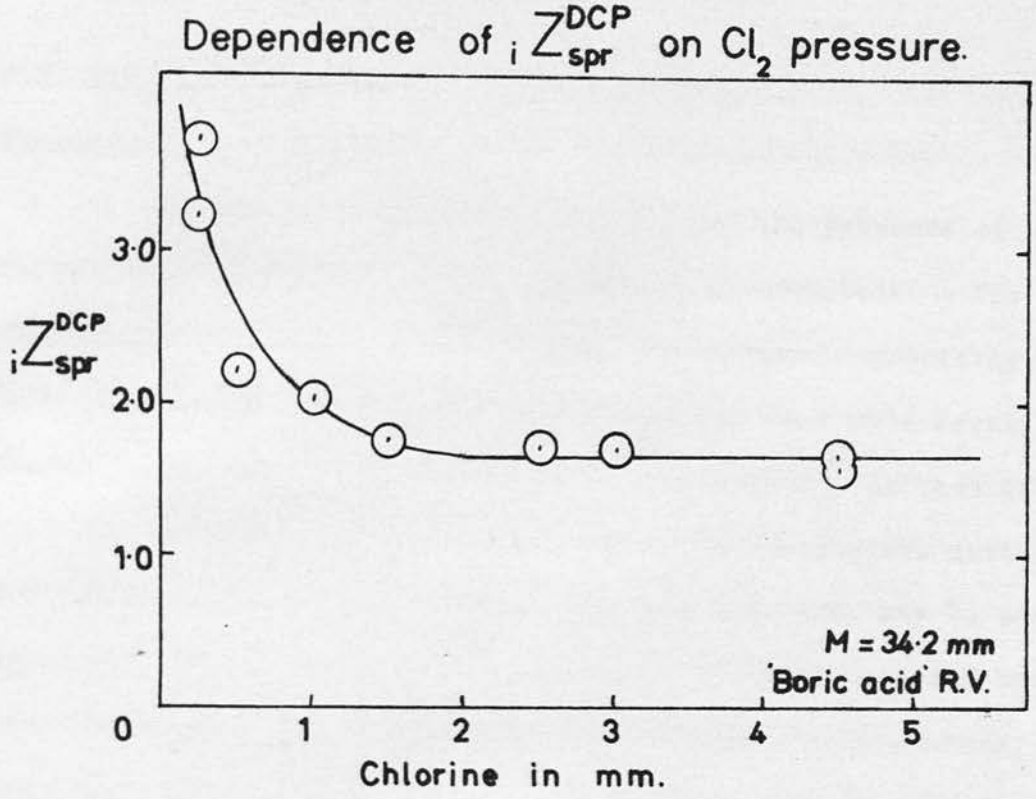
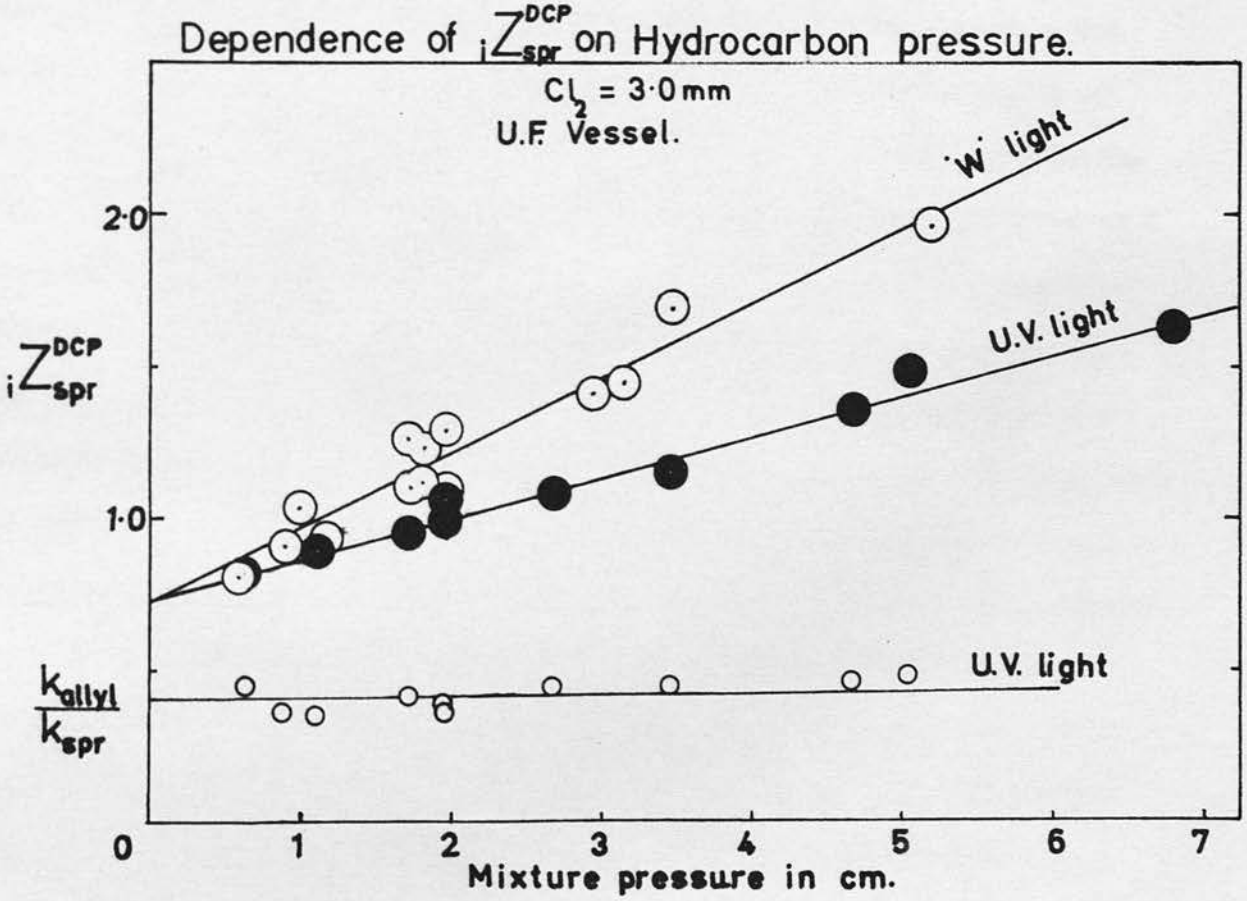


Fig 4.10



4.6 RATE CONSTANTS FROM CHAPTERS 3 and 4.

Evaluation:-

In Chapter 3 evidence was given for the presence of a very rapid 'dark reaction' in the chlorination of isobutene. The present chapter has shown that propylene also chlorinates appreciably in the dark (though less rapidly than isobutene) and that this reaction is probably entirely due to a heterogeneous process. In fact it seems that for the photolytic experiments with propene:propane mixtures, the observed increase in Z^{DCP}_{spr} with mixture pressure, may be adequately explained by the occurrence of concurrent heterogeneous and homogeneous reactions. The corresponding results obtained for isobutene, although less extensive and less reproducible, showed pressure dependencies for the rate of formation of all three products from isobutene. It seems reasonable then to assume that the appreciable 'dark reaction' noted in this system was also a heterogeneous process, and therefore also accounted for the observed pressure dependencies. As the rate of the heterogeneous reaction will decrease with the hydrocarbon pressure it is likely that at very low pressures the rate of the surface reaction will be negligible. Thus the intercepts of the pressure dependence lines, on the Z axis should give true values for the respective rate constant ratios. Such rate constant ratios have been used to calculate the absolute rate constants given in Tables 4.4A and 4.5. The value of k_2 for ethylene has been obtained in a similar manner by temporarily assuming that the dependence on ethylene pressure observed in this system can also be interpreted in the above manner.

As indicated earlier the intersection of the three Log (1+R) v T_d lines obtained at different pressures, for propene, should also

correspond to zero dark reaction and the value of k_2 obtained by this method is shown in Table 4.4A and designated as (b).

From the study of the effects of different surfaces on the propene system it can be seen that the formation of allyl chloride was to some extent surface dependent indicating the presence of a heterogeneous process. However the concentration ratios, Z^{allyl}_{spr} obtained from photolytic experiments were virtually independent of pressure. In this case, then the dark reaction appears to be slow and insignificant in relation to the photolytic reaction and the competitive method should yield accurate values of kallyl/kspr. However it can be seen from Table 4.5 that the value for kallyl obtained from this work using UV light and a Urea Formaldehyde coated vessel is somewhat lower than that obtained from Miss Thomson's work using a 'tungsten' light and a clean glass vessel. This seems to imply, contrary to the above argument, that the surface reaction was significant, but that its contribution to the total reaction was reduced in our work. These conflicting observations can only be reconciled if the surface reaction was independent of olefine pressure, or an analytical error was present in one or other of the investigations.

Addition reactions

Table 4.4A shows that Log k_2 for ethylene obtained by the method given above, is an order of magnitude lower than that for propene or isobutene but is the same as that obtained by Goldfinger et al. for C_2Cl_4: it is somewhat lower than that obtained by Ayscough et al. for cis-dichloroethylene. Transition state considerations suggest that the A factor for chlorine atom addition to ethylene should be 5 to 10 times that for addition to C_2Cl_4 and table 1.1

shows that in fact the experimental values of A for the series $C_2H_{4-n}Cl_n$ do tend to increase with decrease in n. Dainton et al[49] have estimated $Log_{10}A$ for C_2H_3Cl as 10.3 ± 0.6. As n decreases the corresponding bond strength D(A-Cl) increases[46] thus it is not likely that E_2 for ethylene will be larger than that for the chloro-olefines. Goldfinger[57] et al. obtained $E_2 = 0$ for C_2Cl_4 while Dainton et al. obtained a value of 1.2 ± 0.7 k.cal. for cis-dichloro-ethylene. However the former value was obtained from several investigations, some of which employed a competitive technique whilst the latter value was obtained using the difficult rotating sector method. The former value is therefore more likely to be correct. If the true value of E_2 for ethylene is estimated as 500 cal or less then it can be seen that the value of k_2 obtained here for ethylene is low, and it is possible that the activated radical scheme mentioned earlier, is responsible for the pressure dependence in this system. (It should however be pointed out that if E_2 for ethylene is 1 to 2 k.cal as suggested by the value 2 k.cal calculated from Stewart & Wiedenbaum's results[68] then Log A_2 values of 10.3 to 10.6, would explain the Log k_2 value of 9.2. This would allow the expected increase in A whilst suggesting that contrary to expectations E_2 increases from C_2Cl_4 to C_2H_4. However this is not thought to be a likely explanation).

The agreement between the values of Log k_2 for propene obtained in this work using two separate methods, suggests that the interpretation of the pressure dependence in terms of a heterogeneous process was correct for this system. Furthermore the slightly higher value obtained by Miss Thomson is in accordance with there having

been a more significant surface reaction in her uncoated reaction vessel. It seems likely that the analogous interpretation of the isobutene system is also correct.

As can be seen from page 32 there is good reason to beleive that D(A-Cl) increases from ethylene to isobutene. A corresponding decrease in E_2 might therefore be expected and this might account for the observed increase in rate constants. However as already pointed out, a value of E_2 for ethylene of 500 cal or less, is favoured here, and thus if it is assumed that E_2 cannot be negative for this series, increase in rate constant must be almost completely accounted for by a corresponding increase in A factor. In contrast it is interesting to note that for methyl radical addition, Table 4.4C increase in k_2 from ethylene to propylene is entirely due to a decrease in E_2, while the corresponding A factors also tend to decrease.

Little precise work has been done on the addition of either atoms or free radicals to olefines. The most comprehensive studies have been those on alkyl radicals additions, and a review of this work has been recently made by Kerr & Trotman-Dickenson[45]. A few of the results for ethyl radicals have been reproduced here in Table 4.4C and these are typical of the constancy of the rate constants obtained for the reaction of this bulky radical with different unsaturates. In contrast, work on the addition of ^3P O-atoms to olefines (also reviewed in ref 45) has shown a wide variation in the activities of different olefines. Cvetanovic has obtained the relative rate constants for O-atoms addition to ten olefines, taking k isobutene = 1; three of his results are given in Table 44B and where possible the corresponding values from the present work on chlorine atoms are also given.

(Cvetanovic's results were obtained from competitive experiments and are therefore likely to have good accuracy). The concordance of the relative rate constants obtained in this way for the different atomic reactions with ethylene is probably fortuitous however it is interesting to note that the orders of magnitude of the relative rate constants are similar for both atomic species. This apparent correlation conflicts with the conclusion drawn above, that the rate constant obtained here for ethylene is low. A further study of the ethylene system is reported in Chapter 5 and this attempts finally to resolve this problem.

Absolute rate constants for oxygen atom reactions are less accurate, but a value of 4.5×10^9 $l mole^{-1} sec^{-1}$ has been obtained for isobutene, thus the chlorine atom addition reactions take place approximately ten times faster than those for oxygen atoms. Unfortunately no values for the individual Arrhenius parameters have as yet been obtainable for the O-atom additions.

Hydrogen abstraction reactions.

Table 4.5 contains the rate constants obtained here for the abstraction of hydrogen atoms from alkenes, together with a few of those obtained by Knox & Nelson for H· abstraction from alkanes. No A factors or activation energies are known for the abstraction of H-atoms from alkenes but in table 4.5 activation energies are given which have been calculated on the assumption that the presence of the double bond does not significantly alter the A factors per hydrogen atom from those obtained for the corresponding alkanes. On this basis it appears that the presence of the double bond in isobutene has lowered the activation energy for removal

of a primary hydrogen, whilst E_2' for abstraction of a hydrogen atoms from the vinylic = CH_2 group is almost three times larger than that for removal of a primary hydrogen from isobutane. (The A factor for the vinyl abstraction may not be as assumed but it is not thought likely to be less than 0.9×10^{10} which would still mean an increase in E_2'). These observations are in fact what one might expect in view of well known enhanced activity of allylic hydrogen which is caused by hyperconjugation with the double bond and the resonance stabilisation of the insipient free radical. At the same time these effects render the vinylic hydrogen relatively inert. Miss Thomson's value of $Log_{10}k_2'$ for allyl chloride also indicates a slight reduction in the activation energy compared with that for abstraction of a primary hydrogen from propane. However the value obtained for $Log_{10}k_{allyl}$ in this work does not indicate any lowering of the activation energy. This may well be due to an error introduced in the analyses, for as pointed out earlier the alkyl chloride and n propyl chloride products gave one composite peak whose area was assumed to be directly proportional to the sum of the individual components.

The fact that the rate constant for methallyl chloride formation is smaller than that for formation of 1.2 dichloro-isobutane would not be expected at first sight, from the analytical results, for methallyl chloride was almost always the major product. This is explained by fig. 3.6 which shows that the rate of formation of methallyl chloride increased much more rapidly with pressure than did the rate of 1.2 addition. Both pressure dependencies were interpreted as due to surface reactions thus the rate of heterogeneous

addition. A corresponding heterogeneous chlorination of isobutane would not be expected to take place as the olefine is almost certainly held to the surface by means of its double bond in which case one of the hydrogens in each $-CH_3$ group will be very near, if not actually touching the surface. At the same time the two hydrogens of the vinylic H_2 group will have a carbon atom between them and the surface and heterogeneous chlorination of this group seems much less likely. In concordance with this theory the pressure dependence for formation of $\beta\beta$ dimethyl vinyl chloride was very shallow and in view of the irreproducibility in this system, it may not in fact be real.

It was suggested earlier that formation of the vinylic product might be brought about by dehydrochlorination of the initially formed 1.2 dichloro isobutane. However in the reaction scheme for the pyrolysis of 1.2 dichloro ethane Howlett included the step

$$Cl\cdot + C_2H_4Cl\cdot = C_2H_3Cl + HCl$$

for which he obtained $k = 10^{10} \exp(-3000/RT)$ l mole^{-1} sec^{-1}. Now it can be seen from Table 1.1 that even at quite low chlorine pressurea this reaction is unlikely to compete significantly at 308°K with

$$ACl\cdot + Cl_2 = ACl_2 + Cl\cdot$$

It is interesting to note that Howlett used a reaction vessel coated with a carbonaceous film to inhibit surface reaction thus it might have been possible in our clean glass system for dehydrochlorination to take place by surface catalysis. Such a surface reaction could probably produce either $\beta\beta$ dimethyl vinyl chloride or methallyl chloride depending on the orientation of the adsorbed molecule or radical.

TABLE 4.4

A. Rate Constants at 308°K for the reaction

$$A + Cl^{\cdot} = {}^{\cdot}ACl \qquad (2)$$

Olefine	$Log_{10}k_2$	Reference
C_2Cl_4	9.2	47 & 57
$C_2H_2Cl_2$	9.45	39b
C_2H_4	9.2	this work
C_3H_6	(a) 10.21	this work
	(b) 10.17	this work
	10.29	Miss Thomson
iso C_4H_8	10.62	this work

B. Relative Rate Constants for Addition of Atoms to Olefines

Olefine	Relative k, isobutene = 1		
	For $O(^3P)$ at 295°K	For Cl at 308°K	
C_2H_4	0.038	0.038	see reference
C_3H_6	0.23	(a) 0.39	45 page 33
		(b) 0.35	for a review
iso C_4H_8	1.00	1.00	of oxygen atom
2.3 dimethyl butene-2	4.18	-	work (Kaufman)

C. Arrhenius Parameters for Alkyl Radical Addition to Olefines

	E k.cal.	$Log_{10}A$ $l.mole^{-1}sec^{-1}$	$Log_{10}k$ at 308°K	Reference
${}^{\cdot}CH_3$ +				
C_2H_4	7.0	8.2	3.24	105
C_3H_6	6.0	7.8	3.54	105
${}^{\cdot}C_2H_5$ +				
C_2H_4	6.9	8.0	3.10	Reviewed
1-Hexene	6.8	7.9	3.08	in
1-Octene	6.7	7.9	3.15	Ref
2.3.3. Trimethyl-1-butene	5.6	7.2	3.20	45

TABLE 4.5

Absolute Rate Constants for Hydrogen Abstraction Reactions

RH	Product	$Log_{10}k_2'$	$10^{-10}xA_2'$ per H atom	E_2' cal $mole^{-1}$	Reference
C_2H_6	C_2H_5Cl	10.22	1.5 ± 0.2	1040	44
C_3H_8	pC_3H_7Cl	10.30	1.7 ± 0.2	1000	"
C_3H_8	$secC_3H_7Cl$	10.36	3.6 ± 0.5	680	" (Competitive Standard here)
iso C_4H_{10}	p.iso C_4H_9Cl	10.50	1.3 ± 0.2	820	"
			(Assumed)		
C_3H_6	$ClCH_2CH = CH_2$	9.96	1.7	1050	this work
		10.06(42°C)		930	Miss Thomson
iso C_4H_8	CH_3, $ClCH_2$ > $C = CH_2$	10.47	1.3	595	this work
iso C_4H_8	$(CH_3)_2C = CHCl$	8.66	1.3	2480	this work

CHAPTER 5

A further study of the chlorination of ethylene:propene mixtures.

5.1 The 'dark' reaction

Introduction:- The presence of a 'dark' reaction in the ethylene system had not been ascertained in the previous preliminary study. However, initial experiments in the present investigation showed that a reaction mixture, left entirely in the dark, produced quantities of 1.2 dichloroethane but unlike the propene and isobutene systems, no substitution reaction occurred. After about ten minutes dark time, photolysis produced large amounts of n and iso propyl chlorides, and it was at once apparent that the 'dark' reaction was much slower here, than in the other two olefine systems. Consequently a study of the dark reaction alone was feasible for this system and the results of such a study are reported below.

All the work of this chapter was carried out in the same U.F. vessel that was used for the propylene investigation and photolysis was achieved by means of a mercury lamp. Secondary chlorination was more marked in this system thus all Z values are given in terms of total propyl chlorides.

Log $(1+R')$ vs t_d graphs. Exactly the same procedure was used as that already described in detail for propylene (p 107). However as secondary chlorination occurred in some cases, R' was used instead of R.

$$\text{where } R' = \frac{(DCE)}{(\text{Total propyls})}$$

The results for four different chlorine-hydrocarbon mixtures are given in Table 5.1 and Fig 5.1. The gradients of the straight lines portions of

the graphs give the following values for the rate const, k_d, of the dark reaction.

Reactants in mm.

	C_2H_6	C_3H_8	Cl_2	$10^4 x k_d$ min^{-1}	
a	10.4	9.4	2.0	1.95	
b	16.0	14.0	10.0	2.02	
c	69.0	31.4	2.0	7.80	U.V. light - U.F. vessel.
d	69.0	31.4	10.0	7.30	

These can be compared with those values obtained earlier for propylene and corrected here to be in terms of R′.

Vessel	C_3H_6	C_3H_8	Cl_2	$10^4 \times k_d$ min^{-1}	
Pyrex	9.5	10.5	1.5	82	Tungsten Lamp.
U.F.	9.9	8.6	1.5	63	

It can be seen that the 'dark' rate in the ethylene system was virtually independent of chlorine pressure whilst it increased with increase in hydrocarbon pressure. The data is not sufficiently extensive for one to decide whether the ethylene pressure alone, was important in this latter respect, or whether in fact the total hydrocarbon pressure was more aignificant. However it is quite apparent that the 'dark' rate for propylene, in a U.F. vessel using 'tungsten' light, was some thirty times as fast as that for ethylene, in the same vessel using U.V. light.

The graphs obtained at the higher ethylene pressure, although linear after ten minutes 'dark' time, exhibited the 'initial burst' effect discussed on p132-133 with reference to the propylene system. It was suggested then

that this effect might be due to the poisoning of ultra active surface sites, by adsorption of a product and it was argued that although this initial burst was not observed in the propylene 'dark' time graphs, it could still have been present if it was rapid enough to be significant relative to the photolytic reaction at zero dark time. Following from this argument, as the overall 'dark' reaction was slower in the ethylene system it is quite likely that the initial burst was also slower and therefore observable. It was realised that if the limited poisoning theory were correct the initial burst effect should be reduced or eliminated by adding some substance to the R.V. which would be adsorbed on the ultra active sites before a reaction was begun. Thus a series of runs were carried out, in which 15 mm. of cis dichloro ethylene were admitted to the R.V. first, followed by 10 mm. chlorine and a mixture containing 64 mm. ethylene, and 36.5 mm. propane. The resulting $\text{Log}(1 + R')$ v t_d plot fits almost exactly onto the line for the series denoted (d) above, except that the initial burst effect was appreciably reduced. Whilst this reduction was what was hoped-for, the straight line portion of the graph should have been displaced down the $\text{Log}(1 + R')$ axis, by a distance equal to the reduction in the initial burst and the intercept value at $t_d = 0$ should have been about the same as before. The fact that this did not occur was later explained by the catalytic effect which cis-D.E had on the photolytic formation of DCE.(see section 5.2). Further support for the idea of 'poisoning' was obtained by the observation that in the above work secondary chlorination of the mono propyl chlorides was markedly reduced and in most cases completely eliminated by allowing a 'dark' time of five or more minutes. Furthermore the addition of cis-D.E. inhibited secondary

chlorination sompletely even when the reactants were photolysed immediately. Photolysis of propane:chlorine mixtures with or without t_d showed no change in the amount of secondary chlorination produced thus it was concluded that the dichloride formation took place to a large extent on the surface and that this surface reaction was inhibited by adsorption of the 1.2 dichloro product from the olefine, and/or the dichloro propanes themselves.

It is interesting to note that Stewart and Edlund observed an initial burst of reaction lasting 12 seconds in the bromine:ethylene system.[58]

The dark reaction alone was followed for several reactant mixtures. The procedure adopted was to carry out a run in the darkened R.V. in the usual manner and, at intervals, remove samples from the reaction mixture for analyses. All runs were carried out at night and during sampling and analysis the room was in complete darkness except for the small 'Bourdon' light. The samples were measured as pressures in the analytical line and varied in size but were always kept within the range of 0-2 mm. so as not to radically alter the concentrations in the R.V. In reporting the results in Table 5.2, Fig. 5.2, all samples have been corrected to a standard sample size which has been calculated so that the same quantity of chlorine would be removed per sample, from each of the different mixtures. In order to reduce the amount of reaction taking place outside, the R.V. samples were frozen down and analysed immediately after their pressures had been measured,

The graphs in Fig. 5.2 show how the amount of DCE produced varies with t_d for different mixture compositions. All graphs are characterised by relatively rapid increase in DCE during the first 40 minutes followed by a

gradual levelling-off towards a certain 'saturation' concentration. However the 'saturation' point did not correspond to complete removal of chlorine. In fact very little chlorine had been consumed by this stage as subsequent photolysis of the residue in the R.V. produced large amounts of propyl chlorides in quantities very similar to those obtained from reactions where no dark time was allowed (*cf* II and run $2t_d5$). This observation fits well into the idea of a surface reaction which is inhibited by adsorption of the product. This theory is further supported by the results for the dark reaction in the presence of 500 mm. CO_2. where the rate of formation of the DCE product was slower, presumably as a result of preferential adsorption of CO_2. Saturation of the surface with product should have occurred when a certain fixed quantity of DCE had been produced and the graphs should therefore all level-off at the same value of DCE. This appears in fact to be the case, within the limits of experimental error, although graph III gives a rather higher value and run VI containing CO_2 was not followed far enough for the 'saturation' point to be observed. The graphs show that rate of attainment of 'saturation' (and hence the 'dark' rate) increased with increase in mixture pressure and this agrees with the findings from the $\mathrm{Log}(1 + R')$ graphs. With reference to these latter graphs it should be noted that if the dark reaction did, in fact cease at a certain value of t_d, then R' would have been constant, at or above that value, and as a result the $\mathrm{Log}(1 + R')$ v t_d graphs would have been expected to level-off. This phenomenon cannot, however, be observed in any of the graphs in Fig. 5.1 and the lines are straight up to dark times of 160 - 280 minutes. The anomaly can only be explained if the dark reaction did not in fact cease completely. The small samples used in the above investigation made it necessary to employ the most sensitive

range of the detector and the resulting errors may have been sufficient to obscure a continued slow increase in DCE concentration, but the consistency of the results especially in run V does not seem to corroborate this supposition.

TABLE 5.1.

Dependence of $Log(1 + R')$ on t_d

U.V. light - U.F. vessel

Reactants:- C_2H_4 = 10.4 mm, C_3H_8 = 9.4 mm, Cl_2 = 2.0 mm.

Run	sPrCl	pPrCl	Multiple Pr	Total Pr	DCE	$\frac{DCE}{Tpr} = R'$	10x Log(1+R')	t_d
1t_d1	78	59	0	137	15.5	.113	0.46	30
2	80	66	0	146	16.7	.114	0.47	66
3	78	60	0	138	21.4	.155	0.63	162
4	80	64	0	144	12.2	.085	0.36	15
5	78	60	0	138	14.6	.105	0.43	46
6	78	60	0	138	17.5	.126	0.52	122
7	68	59	0	127	24.2	.190	0.76	226
8	100	76	0	176	20.0	.114	0.47	20
9	71	55	0	126	31.0	.246	0.96	276
10	60	50	12	122	7.6	.062	0.26	0
	Reactants:- C_2H_4 = 69.0 mm, C_3H_8 = 31.0 mm, Cl_2 = 2.0 mm.							
2t_d1	56	45	0	101	79.3	.785	2.52	61
2	60	52	0	112	69.5	.626	2.11	11
3	60	45	0	105	74.0	.704	2.31	28
4	46	40	0	86	94.0	1.092	3.20	153
5	49	41	0	90	79.0	.878	2.73	86
6	45	36	14	95	34.8	.366	1.35	0
	Reactants:- C_2H_4 = 69.0 mm, C_3H_8 = 31.0 mm, Cl_2 = 10.0 mm.							
3t_d1	244	204	0	448	434	.970	2.95	118
2	273	228	0	501	363	.724	2.37	28

Run	sPrCl	pPrCl	Multiple Pr	Total Pr	DCE	$\frac{DCE}{Tpr} = R'$	$10x \text{ Log}(1+R')$	t_d
3	189	164	0	353	452	1.280	3.58	207
4	250	178	0	428	316	.739	2.40	12
5	187	142	122	451	191	.422	1.53	0
6	330	249	0	579	378	.635	2.14	5
	Reactants:- C_2H_4 = 16.0 mm, C_3H_8 = 14.0 mm, Cl_2 = 10.0 mm.							
$4t_d1$	303	214	57	574	142	.248	0.96	90
2	303	196	47	546	149	.273	1.05	178
3	285	196	43	524	101	.193	0.77	24
4	303	214	53	570	91	.160	0.65	8
5	194	130	106	430	81.5	.189	0.75	0
	Reactants:- C_2H_4 = 69.0 mm, C_3H_8 = 39.4 mm, Cl_2 = 10.0 mm. + 14.8 mm cis dichloro ethylene.							
$CDEt_d1$	224	198	0	422	348	.825	2.61	78
2	214	178	0	392	252	.643	2.16	6
3	200	175	0	375	388	1.034	3.08	127
4	228	195	0	423	413	.977	2.96	100
5	221	195	0	416	223	.536	1.86	0

TABLE 5.2.

The dark reaction

Sample No.	Sample size (Bourdon cm x 10^2)	t_d	Area DCE	Relative Area
I. (Reactants:- C_2H_4 = 83.5 mm, C_3H_8 = 44.2 mm, Cl_2 = 10.0 mm.)				
Standard Sample 1	30	7	90	90
2	33	51	230	209
3	51	74	355	209

Sample No.	Sample size (Bourdon cm x 10^2)	t_d	Area DCE	Relative Area
II. Reactants:- C_2H_4 = 71.5 mm, C_3H_8 = 38.1 mm, Cl_2 = 10.0 mm.				
1	51	6	41	21
2	52	20	240	120
3	30	41	175	152
4	50	69	350	182
5	70	86	530	197
6	52	107	383	192

Remainder photolysed t_d=139, sPr=240, pPr=202, TPr=442, DCE=437, Log($1+R^r$)= .30

III. Reactants:- C_2H_4 = 170.8, C_3H_8 = 90.6, Cl_2 = 10.0 mm.				
1	51	27	134	155
2	50	45	181	214
3	69	61	300	256
4	56	87	232	244
5	50	109	198	234

Remainder photolysed t_d=120, sPr=168, pPr=160, Tpr=328, DCE=539, Log($1+R^r$)= .422

IV Reactants:- C_2H_4 = 75.7, C_3H_8 = 40.2, Cl_2 = 10.0 mm, CO_2 = 512.2 mm.				
1	190	29	140	102
2	51	44	46	125
3	51	73	77	210
V Reactants:- C_2H_4 = 72.5, C_3H_8 = 41.5, Cl_2 = 11.0 mm.				
1	30	12	119	98.4
2	30	32	224	185
3	35	51	65	188
4	30	68	241	199
5	29	85	228	196

Sample No.	Sample size (Bourdon cm x 10^2)	t_d	Area DCE	Relative Area
6	30	141	243	201
7	29	157	226	194

Remainder photolysed t_d=1377, sPr=56, ppr=50, Tpr=106, DCE=2240, Log(1+R´)=1.34

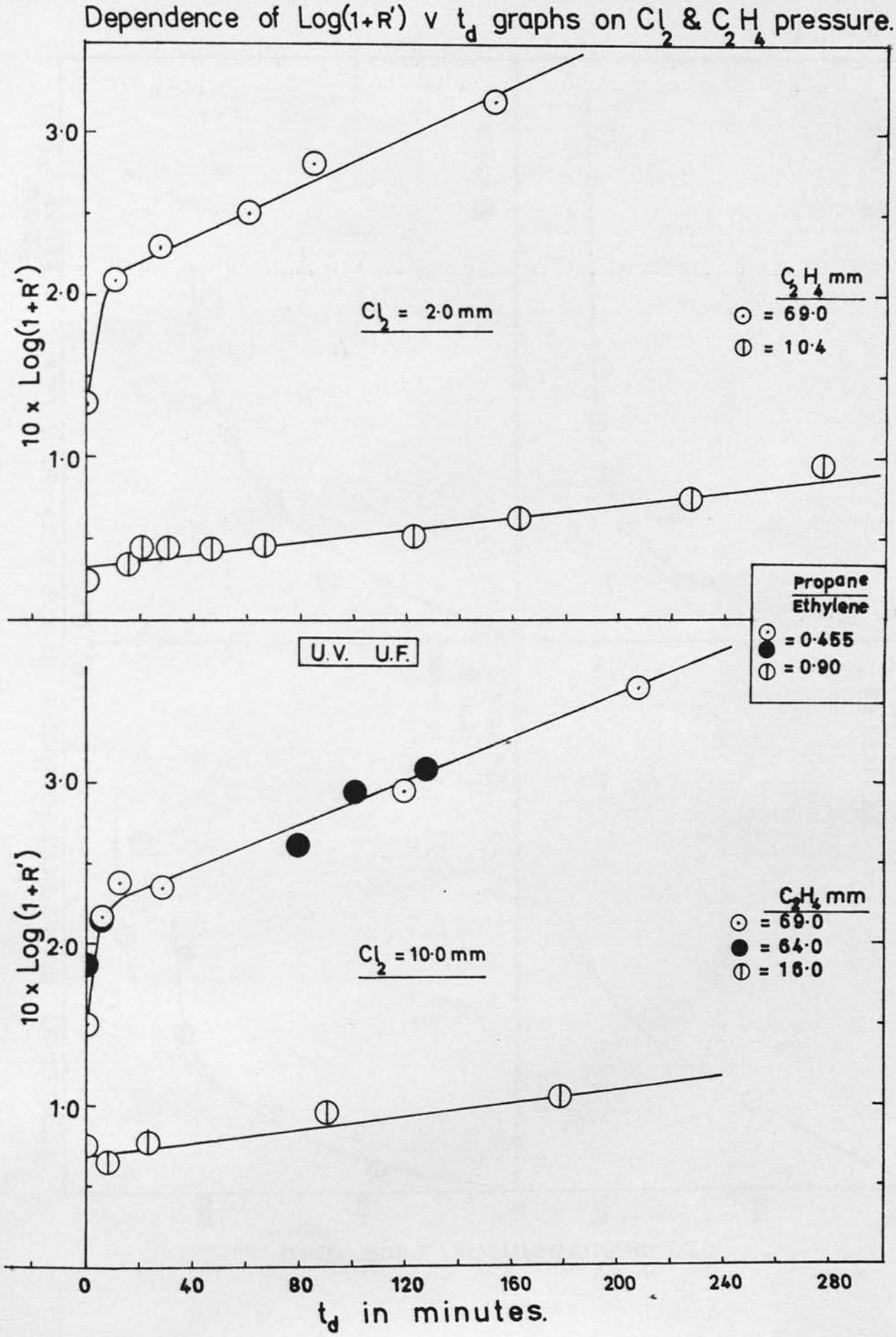

Dependence of Log(1+R') v t_d graphs on Cl_2 & C_2H_4 pressure.
10 x Log(1+R')
3·0
2·0
1·0
Cl_2 = 2·0 mm
C_2H_4 mm
⊙ = 69·0
◑ = 10·4
Propane / Ethylene
⊙ = 0·455
● = 0·90
◑ = 0·90
U.V. U.F.
10 x Log (1+R')
3·0
2·0
1·0
Cl_2 = 10·0 mm
C_2H_4 mm
⊙ = 69·0
● = 64·0
◑ = 16·0
0
40
80
120
160
200
240
280
t_d in minutes.

Fig 5.1

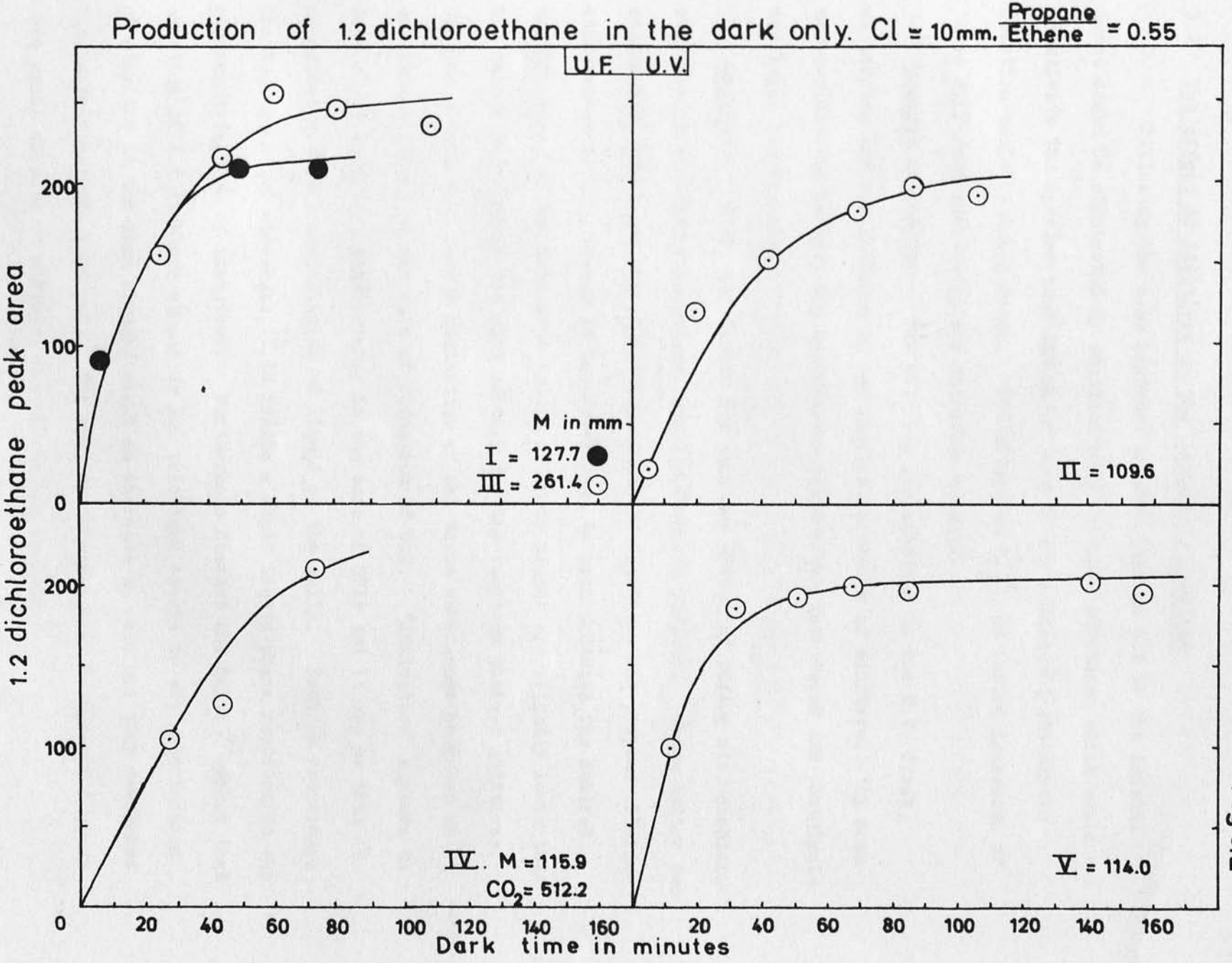

Production of 1.2 dichloroethane in the dark only. Cl = 10 mm. Propane/Ethene = 0.55
U.F. U.V.
1.2 dichloroethane peak area
M in mm
I = 127.7
III = 261.4
II = 109.6
IV. M = 115.9
CO2 = 512.2
V = 114.0
Dark time in minutes
0
100
200
20
40
60
80
100
120
140
160

Fig 5.2

5.2 The effect of Additives on the photolytic reaction

Following the same argument as that used in 5.1 if the initial burst could be eliminated by addition of a suitable substance which would deactivate the surface then the major part of any subsequent photolytic reaction would be homogeneous. The effect on Z^{DCE}_{Tpr}, of varied pressures of three different additives, was therefore studied.

General procedure:- The chlorine was admitted to the R.V. first, as before, and was followed by the required pressure of additive. As soon as possible thereafter, the hydrocarbon mixture was introduced and photolysis was begun immediately.

Results:- Figs. and Tables 5.3 show the effect of adding cis. dichloroethylene, 1.2 dichloro isobutane, and 1.2 dichloro propane. These latter two substances, which are the addition products of isobutene and propene chlorination respectively, appear at low pressures, to have produced the desired deactivation, as the intercept values of their graphs are slightly lower than the values reported in the next section for the reaction without additives. However addition of larger quantities of all three substances produced an activation effect on the rate of formation of DCE. 'Activation' appears to come about abruptly, particularly in the case of DCIB and it may be that it coincides with the condensation of liquid on the walls. Such an occurrence has been reported elsewhere,[74] to induce a rapid liquid phase reaction in the photochlorination of isobutene. Furthermore Stewart and Smith [61] noted that addition of 1.2 dichloro ethane or 1.1.2 trichloro ethane to the chlorination of ethylene in the dark brought about an increase in rate and they concluded that auto-catalysis occurred. The results obtained here do however suggest that small amounts of additive deactivate the surface.

It is particularly interesting to note that the amount of multiple chlorination of propane was progressively reduced as the pressure of additive was increased and in all three cases 5 mm. of additive were sufficient to completely inhibit multiple chlorination. This agrees well with the conclusions of the previous section.

Analytical difficulties were experienced in the above investigations when high pressures of DCP or DCIB were used. The large quantity of high boiling substance tended to act as a 'plug' in the chromatography column and caused distortion of all the peaks which were eluted before it. The difficulty was successfully obviated by analysing the products from such a run, in several portions. The results from the analysis of each portion were then averaged to give the final value (see DP 3 & 11).

TABLE 5.3

The effect of additives

Cis-dichloro ethylene

Reactants:- C_2H_4 = 63.5 mm, C_3H_8 = 36.2 mm, Cl_2 = 10 mm.

Run	Additive in mm	sPrCl	pPrCl	Multiple pr	Total pr	DCE	10x Z^{DCE}_{Tpr}
1CDE 1	14.7	143	107	0	250	194	3.53
2	0	196	160	126	482	151	1.78
3	2.3	187	143	49	379	122	1.83
4	7.5	125	107	0	232	107	2.63
5	11.4	178	150	0	328	165	2.96
6	20.9	172	146	0	318	159	2.85
7	25.1	172	140	0	312	165	3.02
	Reactants:- C_2H_4 = 18.5 mm, C_3H_8 = 10.5 mm, Cl_2 = 2.0 mm.						
2CDE 1	22.7	200	160	0	360	107	1.69
2	10.2	260	234	0	494	122	1.41
3	15.5	54	60	0	94	23.3	1.41
4	0	390	285	29	704	70	0.89

1.2 Dichloro-isobutane

Reactants:- C_2H_4 = 63.5 mm, C_3H_8 = 36.2 mm, Cl_2 = 10 mm.

DCIB 1	2.70	239	199	57	495	125	1.44
2	9.10	147	119	0	266	79.6	1.71
3	11.4	151	122	0	273	97.2	2.03
4	15.1	49	40	0	89	48.6	3.11
5	18.7	78	62	0	140	74.4	3.03
6	12.7	117	100	0	217	69	3.18
7	6.3	212	174	14	400	118	1.68
8	2.0	230	187	53	470	117	1.42

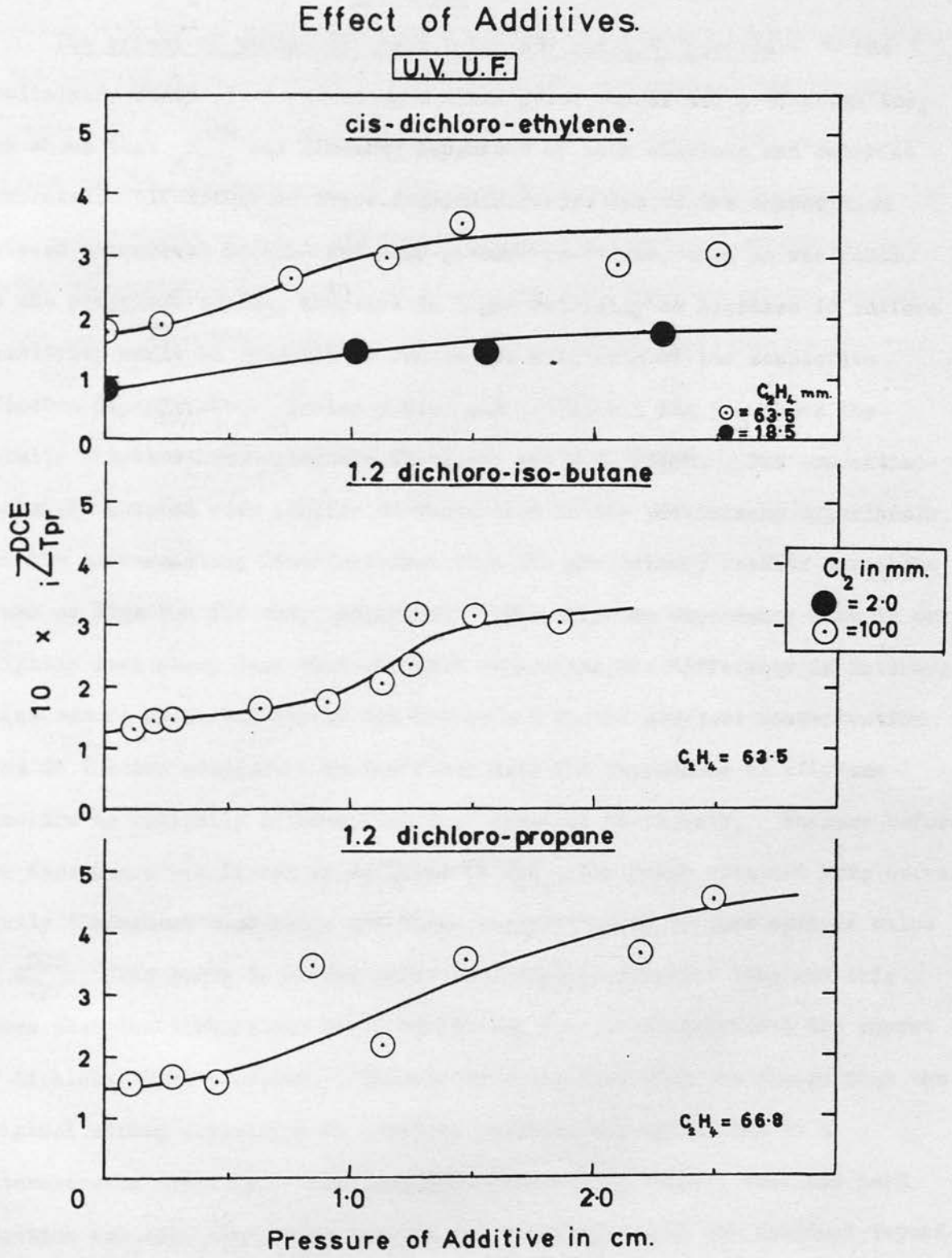
Run	Additive in mm	sPrCl	pPrCl	Multiple pr	Total pr	DCE	10x Z^{DCE}_{Tpr}
9	1.2	230	195	55	480	115	1.37
10	12.5	139	128	35.5	358.5	157	2.33

1.2 Dichloro propane

Reactants:- C_2H_4 = 66.8 mm, C_3H_8 = 38.0 mm, Cl_2 = 10 mm.

DCP 1		4.6	161	135	0	296	80.6	1.55
2		2.7	202	166	36	404	117	1.65
3	a	14.8	89	72	0	161	102	
	b		62	53	0	115	72.8	3.63
	c		102	89	0	191	123	
4		25.2	271	247	0	518	413	4.55
5		8.6	77	62	0	139	84.5	3.46
6	a	11.4	108	98	0	206	77.7	2.16
	b		89	72	0	161	61.1	
7		1.0	212	175	50	437	120	1.56
8	a	21.9	125	107	0	232	146	
	b		80	75	0	155	91.4	3.63
	c		127	100	0	227	157	

Fig 5.3


Effect of Additives.
U.V. U.F.
cis-dichloro-ethylene.
1.2 dichloro-iso-butane
1.2 dichloro-propane
C_2H_4 mm.
⊙ = 63·5
● = 18·5
Cl_2 in mm.
● = 2·0
⊙ = 10·0
C_2H_4 = 63·5
C_2H_4 = 66·8
10 x $i\angle_{Tpr}^{DCE}$
Pressure of Additive in cm.
0
1·0
2·0
1
2
3
4
5

5.3 The dependence of the rate of the photolytic reaction on reactant pressures

The effect of change in light intensity and R.V. surface:- The preliminary study (3.1) and using a clean pyrex vessel and a tungsten lamp had shown that $_{m}Z^{DCE}_{Tpr}$ was linearly dependent on both ethylene and chlorine pressures. If either of these dependences were due to the competition between concurrent hetero- and homo-geneous reactions, then as was found in the propylene system, increase in light intensity or decrease in surface reactivity would be expected to reduce the gradients of the respective pressure dependences. Tables 5.4(a) and 5.5(a) and Fig 5.4 shows the results obtained here using the UF vessel and U.V. light. The concentration ranges covered were similar to those used in the preliminary experiments, and the corresponding lines obtained from the preliminary results have been drawn on Figs 5.4 for easy comparison. The chlorine dependence line is only slightly less steep than that obtained before and the difference in intercept value can be accounted for by the difference in the ethylene concentration used in the two studies. On the other hand the dependence on ethylene pressure is radically altered from that obtained previously. Whereas before the dependence was linear up to 70 mm of C_2H_4, the graph obtained here curves gently throughout that range and tends asymptotically to some optimum value of Z^{DCE}_{Tpr}. The curve is always below the original straight line and this shows that the combination of UF vessel and U.V. light decreased the amount of dichloroethane produced. This is in accordance with the theory that the original strong dependence on ethylene pressure was partly due to a heterogeneous reaction. The dark time graphs (5.1) showed that the dark reaction was very slow under the present conditions thus the residual dependences may well be explained in terms of the activated free radical scheme

(p.102 and below). As we have already seen the theory of this scheme predicts that the extrapolation to zero reactant pressures should give Z = 0. As the surface which depicts the dependence of Z on ethylene and chlorine pressures is no longer flat, its equation cannot be easily obtained. However the low pressure part of the ethylene dependence can be approximated to a straight line as shown and hence the low pressure part of the surface can be considered to be flat. As in the previous case use of the gradients of the two pressure dependences gives the equation of the plane in the form

$$10x_m Z^{DCE}_{Tpr} = 0.27\ (C_2H_4) + 0.50\ (Cl_2) + C$$

The plane goes through the cross plot of the two graphs

thus $10x_m Z^{DCE}_{Tpr} = 0.27 \times 1.60 + 0.50 \times 0.2 + C = 0.70$

therefore $C = 0.17 = 10xZ$ at $Cl_2 = 0$, $C_2H_4 = 0$.

This is a maximum value of the intercept as the ethylene dependence obviously continues to curve downwards, but nevertheless it is about half the value obtained for the clean glass system and suggests that only the activated radical effect was important under the conditions used for this present investigation.

More detailed pressure dependences:

Application of the activated radical scheme outlined on p. 102 to the ethylene system requires that reaction 2 (Appendix A) be replaced by

$$C_2H_4 + Cl\cdot = \cdot C_2H_4Cl^* \qquad 2^*$$

$$\cdot C_2H_4Cl^* = C_2H_4 + Cl\cdot \qquad a$$

$$Cl_2 + \cdot C_2H_4Cl^* = \cdot C_2H_4Cl + Cl_2 \qquad c$$

Deactivation

$$M + \cdot C_2H_4Cl^* = \cdot C_2H_4Cl + M \qquad d$$

This scheme is somewhat different to that proposed by Ayscough et al.[39a] to explain the results for the isomerisation of the dichloroethylenes. Steps a and c correspond to Ayscough's steps α and γ but step β, which was of

the form

$$ACl^{*} + Cl_2 \overset{\beta}{=} A + Cl_3$$

and produced isomerisation in Ayscough's system, has been neglected. Ayscough et al. believed that at their concentrations the most likely outcome of a corresponding collision with an olefine molecule would be a chlorine atom exchange, thus:-

$$ACl^{*} + A \overset{\delta}{=} A + ClA^{*}$$

However there is no reason why such a collision should not also lead to deactivation, particularly under the conditions used here, where the chlorine concentrations were very small compared with the olefine concentrations. Hence in our scheme step d has been included, where M is any molecule other than chlorine (step 8 may also occur but will not affect the concentration of ACl^{*} and can therefore be disregarded).

The above scheme yields the following equation.

$$m^{Z^{DCE}_{Tpr}} = \frac{k_2^{*}}{k_2'}\left[\frac{k_c(Cl_2) + k_d(M)}{k_a + k_c(Cl_2) + k_d(M)}\right]$$

This predicts that Z will depend on both (Cl_2) and (M) at low concentrations of each reactant but will become independent of concentration at higher pressures when it will give a true value of k_2^{*}/k_2'.

Tables 5.4(b) 5.4(c) & 5.5(b) and Figs 5.5 and 5.6 show the results of a more extensive investigation of the effect on Z of change in reactant pressures. The chlorine dependence was studied at a total hydrocarbon pressure of 304 mm, which allowed a greater range of chlorine pressures to be used, whilst the dependence on ethylene pressure was studied at a chlorine pressure of 10 mm. It can be seen that both graphs exhibit the form predicted above. They do not, however, level off at the same value of Z

although the ethylene dependence after an initial steep rise continues to rise gradually over the range 100 to 725 mm and may in fact finally approach the same limiting value as the chlorine dependence. The concentrations at which the limiting value is neared depend on the relative sizes of k_c, k_d and k_a. As Z becomes independent of Cl_2 pressure much more rapidly than it does of ethylene pressure, k_c must be larger than k_d ie chlorine is a better deactivator than is the hydrocarbon. Dainton et al.[48] believe that the lifetime of the $\cdot C_2H_4Cl^*$ radical is somewhat less than 10^{-8}sec. thus $k_a \geqslant 10^8 sec^{-1}$.

It has been assumed above that only the ethylene part of the hydrocarbon mixture was important in the deactivation step d. This particular investigation was carried out using hydrocarbon mixtures of constant composition thus the unimportance of propane pressure was not confirmed here. However in the preliminary investigation the propane/olefine ratio was varied over a wide range without effecting the linear dependence on ethylene pressure and it is therefore thought that the above assumption is justified. It may be that deactivation and chlorine atom exchange take place together, in which case propane would be ineffective.

Experimental The general procedure used in the above investigation was the same as that of earlier work except that mixtures of up to two atmospheres pressure were made up in the mixing vessel. Such high pressures could only be handled in the 'Hone' valve section of the apparatus thus the hydrocarbons had to first be transferred from the storage bulbs to a trap in the metal-tap system. A 2 atmosphere mercury manometer was used for pressure measurements.

Analysis:- Analytical difficulties were experienced because of the high pressures of reactants. The chromatography system had not originally been built to cope with large injections and a special procedure had to be used.

The entire contents of the RV. were first frozen down in liquid nitrogen trap to ensure no air was present. The excess ethylene and propane were then very slowly distilled off. This was accomplished by first replacing the liquid nitrogen trap by a Dewar vessel which had previously been washed out with liquid nitrogen, and then gently warming the 'Dewar' by blowing into it. The rise in temperature could be easily controlled. The evolved gases were allowed into the lower line where their rise in pressure could be followed on the Bourdon gauge. Ethylene distilled off rapidly with very little warming but only a pressure of 5 - 10 cm was allowed to build up before the inlet to the trap was closed and the liquid nitrogen 'Dewar' was replaced. The line was then pumped-out. This procedure was repeated successively until sufficient excess reactants had been removed. With practice it was found that the rate of increase in pressure could be used to indicate how much excess ethylene was present and distillation was usually discontinued when the pressure failed to rise rapidly to about 5 cm. The procedure required care as too-rapid warming caused loss of mono propyl chlorides and it was for this reason that an acetone CO_2 trap could not be used.

The higher chlorine pressures used in this investigation caused more secondary chlorination to take place than heretofore and the column headed 'Multiple pr' in the tables refers to the sum of the 2.2, 1.1, 1.2 and 1.3 dichloro propane products. Table 5.4(c) gives some typical analytical results in detail. At the highest chlorine pressures a little 1.1.2. trichloro ethane was also produced and to avoid error the area of its peak was added to that of the 1.2 DCE peak. As has been mentioned in chapter 2 the columns used for the majority of the analyses did not completely separate some of the dichloro propanes from the other products and in the worst cases approximations

had to be made. However, near the end of this work certain runs were analysed on a column giving complete separation, and it can be seen from the graphs that the results from these analyses agree well with those from the other columns.

TABLE 5.4(a)

The dependence of the photolytic rate on chlorine pressure

Reactants:- C_2H_4 = 16.0 mm, C_3H_8 = 14.0 mm. UV light, UF vessel

Run	Cl_2 in mm. Hg	sPrCl	pPrCl	Multiple pr	Total pr	DCE	$10x_m Z^{DCE}_{Tpr}$
1 ECl 1	12.0	272	196	157	625	126	1.21
2	9.8	194	130	106	430	81.5	1.23
3	16.2	362	209	243	814	200	1.27
4	6.5	200	170	34	404	48.5	0.85
5	3.4	120	102	13	235	23.3	0.78
6	8.0	196	142	73	411	58.3	0.96
7	5.0	140	114	32	286	31.6	0.83
8	1.0	123	107	2	232	15.5	0.57
9	2.0	390	285	29	704	70.0	0.82
10	6.0	184	138	29	351	44.7	0.92

5.4(b)

Reactants:- C_2H_4 = 184.0 mm, C_3H_8 = 97.5

2 ECl 1	20.0	303	205	256	764	441	2.92
2	30.0	480	392	279	1151	740	3.20
3	40.0	676	534	374	1584	961	2.93
4	50.0	499	356	406	1261	934	3.54
5	50.0	544	400	342	1286	925	3.44
6	14.9	290	200	127	617	272	2.34
7	25.0	400	285	188	873	486	2.78
8	2.5	197	147	111	455	133	1.55
HP18	10.0	236	176	125	537	194	1.91
2 ECl 9	5.0	97	80	121	298	53	0.94

5.4(c)

Reactants:- C_2H_4 = 184.0 mm, C_3H_8 = 97.5 mm.

Run	Cl_2 mm	sPr	pPr	Multiple pr. 2.2	1.1	1.2	1.3	Total pr	DCE	$10x_m Z_{Tpr}^{DCE}$
2 ECl 10	20.0	365	265	48	20	97	36	831	365	2.22
11	40.0	596	419	75	39	168	86	1383	982	3.48
12	1.5	200	167	8	12	29	0	416	88.4	1.13
13	30.0	510	365	61	31	129	45	1141	692	3.03
14	7.5	150	118	17	8	37	10	340	125	1.92
15	10.0	200	156	20	8	41	13	438	158	1.85

TABLE 5.5(a)

The dependence of the phololytic rate on hydrocarbon pressure

Chlorine pressure = 2.0 mm. $\frac{\text{Propane}}{\text{Ethane}}$ =0.90 for E1 to E11 and 0.46 for E12 to E14

Run	C_2H_4 in mm	sPrCl	pPrCl	Multiple pr	Total pr	DCE	$10x_m Z_{Tpr}^{DCE}$
E 1	8.1	56	46	14	116	8.4	.57
2	15.8	68	48	9	125	8.6	.62
3	19.6	78	56	12	146	13.3	.82
4	24.5	56	44	13	113	10.2	.81
5	17.3	64	55	8	127	11.0	.78
6	25.9	64	55	10	129	11.6	.81
7	9.2	73	56	7	136	9.4	.55
8	8.0	73	59	7	139	9.4	.54
9	28.8	64	58	10	132	15.1	1.03
10	49.0	185	147	94	426	58	1.22
11	10.3	60	50	12	122	7.6	0.51
12	66.6	50	36	10	96	30.1	1.43
13	68.8	45	36	14	95	34.8	1.66
14	41.6	200	153	25	378	65.0	0.92

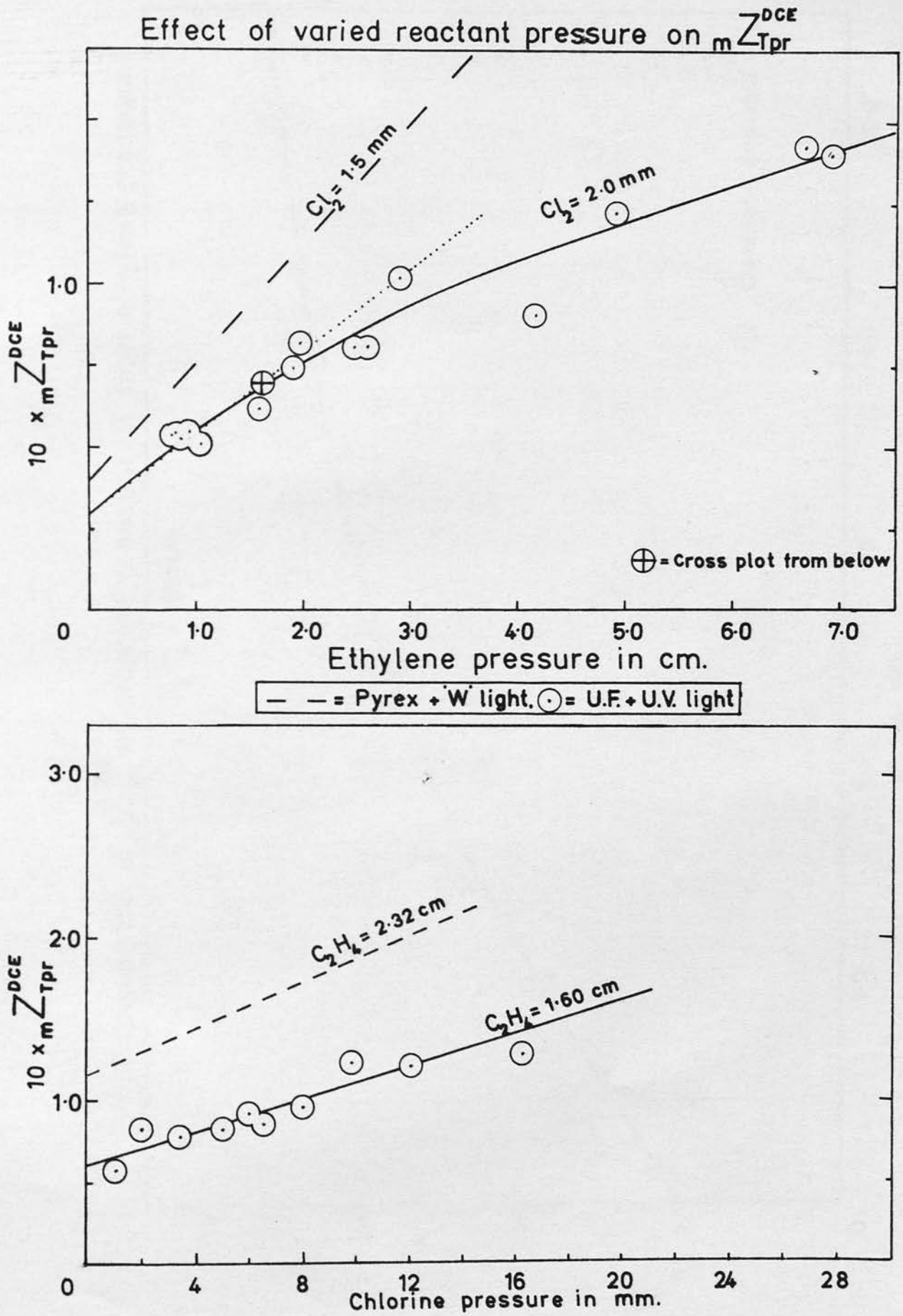
TABLE 5.5(b)

Chlorine pressure = 10.0 mm, $\frac{\text{Propane}}{\text{Ethene}}$ = 0.53

Run		C_2H_4 in mm	sPrCl	pPrCl	Multiple pr	Total pr	DCE	$10x_m Z^{DCE}_{Tpr}$
2E	1	49.5	228	173	95	496	183	1.72
	2 a	730.0	207	173	98		210	
	b		20	10	0	538	10	2.52
	c		2	28	0		36	
	3	645	180	173	77	430	193	2.38
	4	563	180	173	88	441	208	2.50
	5	499	180	160	105	445	208	2.48
	6	436	210	164	109	483	190	2.08
	7	383.5	179	126	88	393	166	2.24
	8	52.5	220	176	116	512	203	1.88
	9	327.5	207	153	112	472	208	2.34
	10	292	176	140	81	397	164	2.19
	11	249	233	175	101	509	207	2.16
	12	31	234	165	141	540	197	1.63
	13	216	232	156	109	497	186	1.98
	14	165	230	168	104	502	175	1.85
	15	144	217	162	110	489	197	2.14
	16	126	242	184	115	541	193	1.89
	17	101	223	162	112	497	200	2.03
	18	188	236	176	142	554	200	1.91
	19	92	221	116	106	487	189	1.94
	20	62	230	167	105	502	191	1.84
	21	54	225	175	122	522	194	1.76
	22	47.3	220	165	105	490	171	1.62

Run	C_2H_4 in mm	sPrCl	pPrCl	Multiple pr	Total pr	DCE	$10x_m Z^{DCE}_{Tpr}$
23	40	217	157	103	477	174	1.63
24	34	224	172	105	501	181	1.59
25	44.5	232	175	103	510	185	1.68
26	52	230	173	101	504	171	1.61
27	38	226	150	102	478	178	1.67
28	112	232	167	85	484	188	1.97
29	101	213	167	105	485	185	1.91
30	218	190	150	97	437	185	2.26
31	248	192	148	89	429	177	2.20

Fig 5.4


Effect of varied reactant pressure on $_mZ^{DCE}_{Tpr}$
Cl_2 = 1·5 mm
Cl_2 = 2·0 mm
⊕ = Cross plot from below
$10 \times {}_mZ^{DCE}_{Tpr}$
1·0
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
Ethylene pressure in cm.
— — = Pyrex + 'W' light, ⊙ = U.F. + U.V. light
C_2H_4 = 2·32 cm
C_2H_4 = 1·60 cm
3·0
2·0
1·0
0
4
8
12
16
20
24
28
Chlorine pressure in mm.

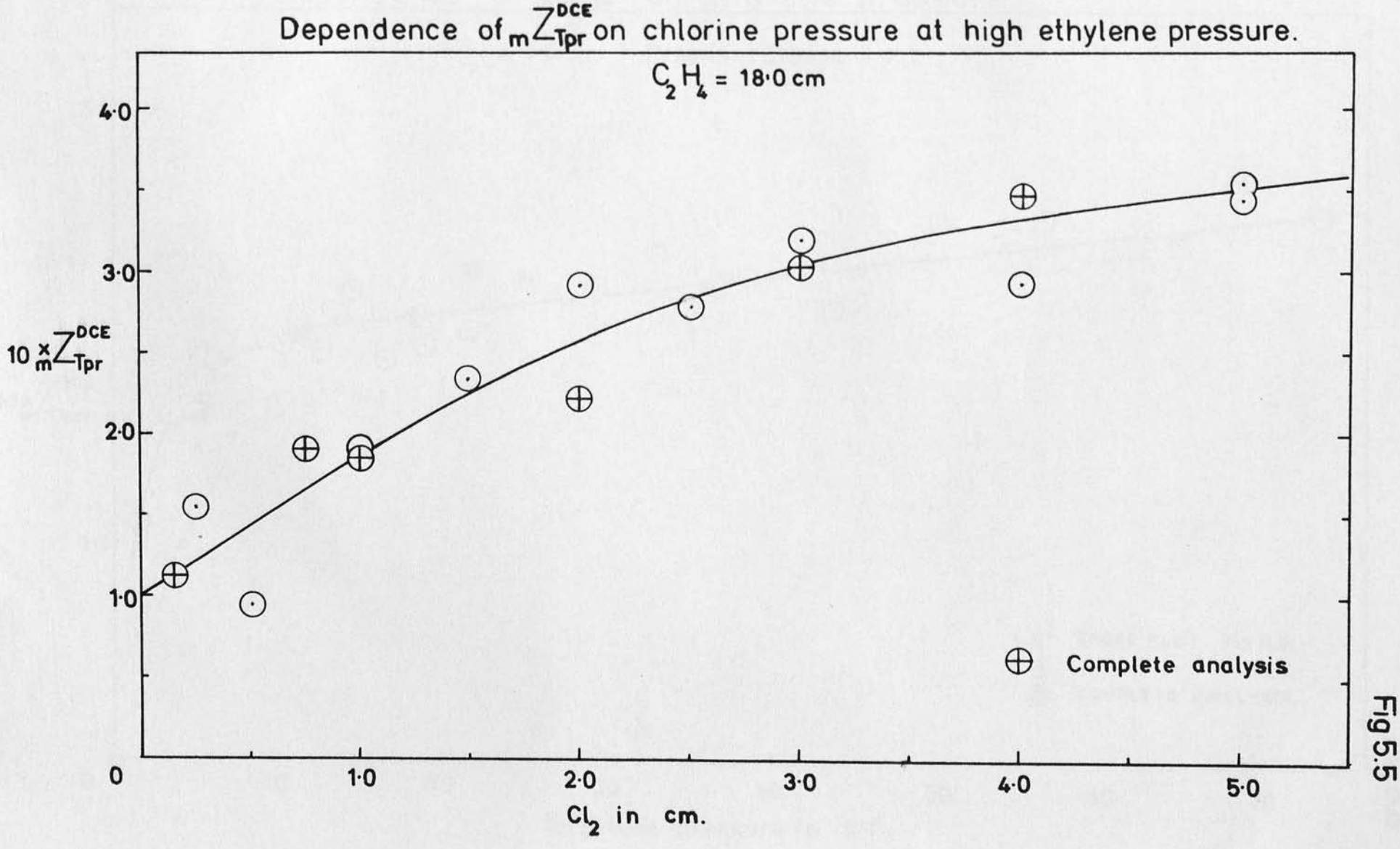

Dependence of $_{m}Z^{DCE}_{Tpr}$ on chlorine pressure at high ethylene pressure.
C_2H_4 = 18·0 cm
$10\ {}^{x}_{m}Z^{DCE}_{Tpr}$
4·0
3·0
2·0
1·0
0
1·0
2·0
3·0
4·0
5·0
Cl_2 in cm.
Complete analysis

Fig 5.5

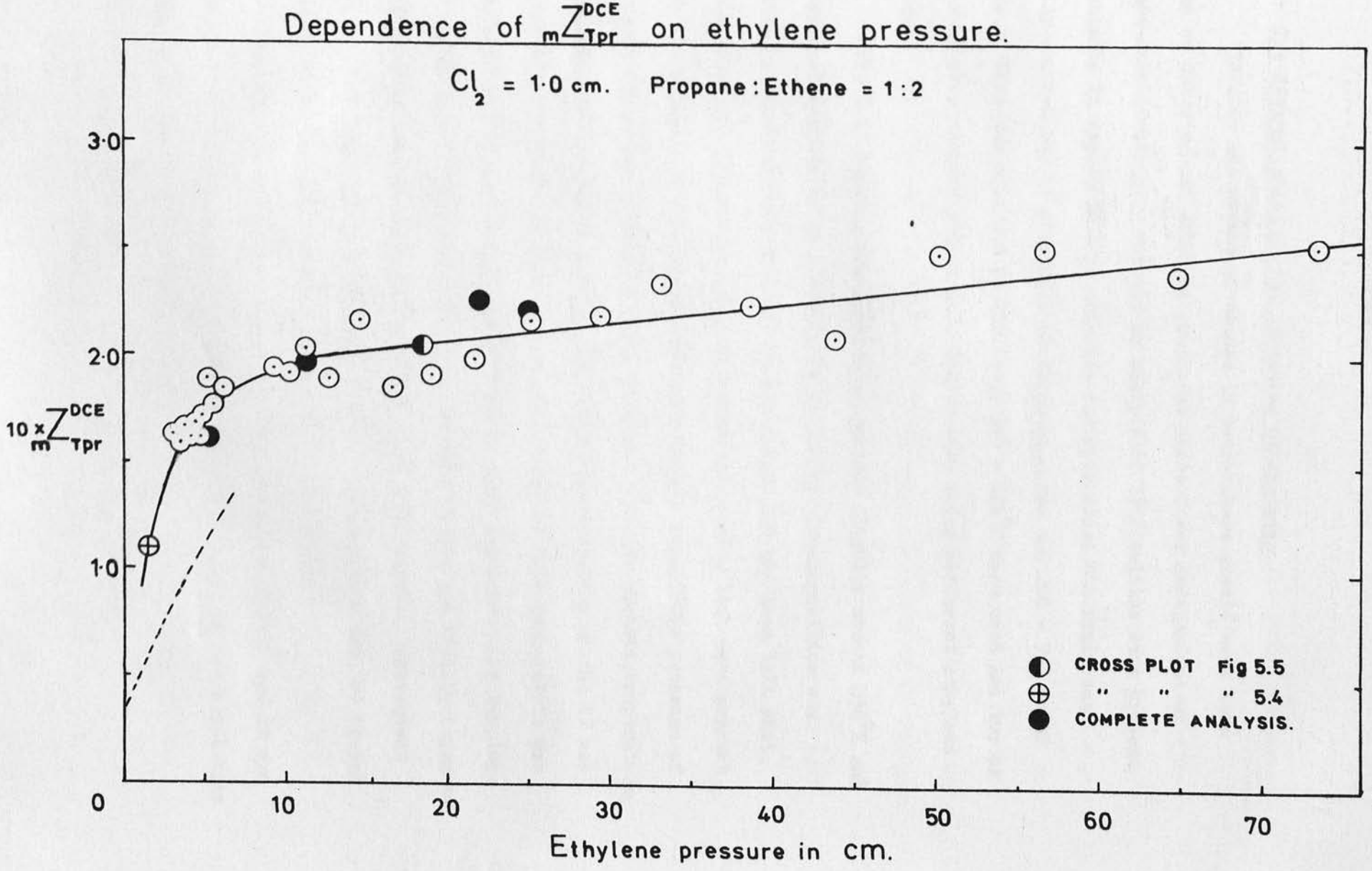

Dependence of $_mZ^{DCE}_{Tpr}$ on ethylene pressure.
Cl_2 = 1·0 cm. Propane : Ethene = 1 : 2
$10 \times {}_mZ^{DCE}_{Tpr}$
3·0
2·0
1·0
0
10
20
30
40
50
60
70
Ethylene pressure in cm.
CROSS PLOT Fig 5.5
" " " 5.4
COMPLETE ANALYSIS.

Fig 5.6

5.4 The determination of the Arrhenius parameters.

Ideally the effect of change in temperature should have been studied at chlorine and ethylene pressures where Z was independent of reactant concentration. However as analytical difficulties were present particularly in regard to high chlorine concentrations the study was actually carried out at pressures of 25 mm chlorine and 200 - 700 mm of ethylene. Nine temperatures in the range 20° - 184°C were used and two or three runs were carried out at each temperature using different ethylene pressures.

The U.F. coating was found to decompose slightly around 350°K and the decomposition was quite appreciable at 450°K. Decomposition was indicated by the fact that when the RV was pumped out and then left shut, for a few minutes, a pressure built up inside it as if a leak were present. However the gases could be frozen down and analysis showed the presence of up to seven components mostly in small amounts. At the highest temperature, 457°K, gases were evolved so rapidly that complete evacuation of the RV was not possible; furthermore some of the gas evolved at this temperature was non condensable and was thought to be Nitrogen from the urea. On keeping the RV at 457°K for 1 hr. the coating became dark yellow and finally began to peel-off. This process was greatly enhanced by U.V. light. Subsequent cooling to room temperature prohibited further decomposition and the vessel could once again be easily pumped out to 10^{-5} - 10^{-6} mm Hg.

In Fig 5.7 Log Z_{DCE}^{Tpr} has been plotted against $(1/T)\times10^{3}$ and it can be seen that the resulting graph is curved instead of being the straight line required by the normal Arrhenius equation

$$\text{Log}_{10}\frac{k_{Tpr}}{k_2} = \text{Log}_{10}\frac{A_{Tpr}}{A_2} + (E_2 - E_{Tpr})/2.303RT$$

It cannot therefore be interpreted directly to give the Arrhenius parameters for k_2. It was noticed that the total products formed, decreased with increase in temperature and this was at first thought to be due to interaction with the heated urea resin. However a constant pressure of chlorine was used throughout the investigation thus the actual concentration of chlorine in the RV decreased with increase in temperature. Fig 5.8 shows a plot of total products v temperature. Also plotted are the corresponding values for the total products calculated on the assumption that the chlorine almost instantly heated to RV temperature on admission. (ie the chlorine heated to RV temperature in the time it took for the gas to be admitted and the pressure to equilibrate - about 5 to 10 seconds) The total products at 294°K were used as the standard for these calculations.

The graph shows good correlation between theory and experiment except for the last point at 457°K where decomposition of the coating was rapid. Loss of products does not therefore account for the curvature of the Arrhenius plot. On the other hand increase in temperature decreased the amount of chlorine and ethylene entering the RV, and as Z depended on both reactant concentrations this will certainly have affected the results. For instance at 457°K introduction of a pressure of 263 mm of C_2H_4 and 25 mm Cl_2 would correspond to 177 mm and 16.8 mm respectively, at 308°K. The fall in Z^{DCE}_{Tpr} as a result of the fall in ethylene pressure would have been negligible but on the basis of the chlorine dependence graph at 308°K, the fall in chlorine concentration would have decreased 10 x Z^{DCE}_{Tpr} by about 0.4. This is not however sufficient to account entirely for the curvature of the $10 \times Z^{Tpr}_{DCE}$ v $(1/T)10^3$ graph and some other process must have been operative.

Calculation and interpretation.

In order to interpret the graph the curvature was attributed to a

combination of two processes one which predominated at low temperature with a rate constant k_x and the other which predominated at high temperature with rate constant k_y. Both processes would occur over the entire range of temperature thus the curve corresponds to a plot of $\text{Log}(k_x + k_y)$ v $1/T$. The two separate straight lines which would have been obtained had these processes been independently observable, were estimated in the following manner.

By inspection two lines were drawn, one corresponding to Log k_y v $1/T$, which was as near as possible asymptotic to the experimental curve at high temperature, and the other corresponding to Log k_x v $1/T$ which was nearly asymptotic to the curve at low temperature. The values of Log k_x and Log k_y at various temperatures were then read directly from the graph and thus the corresponding graph of $\text{Log}(k_x + k_y)$ v $1/T$ was easily obtained (Table 5.7). The gradients of the straight lines were then adjusted and the procedure was repeated till the composite curve gave a 'best fit' to the experimental points. The low temperature contributor to the curve was taken as the true graph of $\text{Log}_{10} \frac{k_{Tpr}}{k_2}$ v $1/T$ which would have been obtained, if perturbing effects had not been present. The experimental curve and the component lines are given in Fig 5.7

Now

$$\frac{k_{Tpr}}{k_2} = \frac{k_{spr} + k_{ppr}}{k_2}$$

$$k_{spr} = 10.2 \times 10^{10} \exp(-1000/RT)$$

$$k_{ppr} = 7.2 \times 10^{10} \exp(-680/RT)$$

and as the Arrhenius parameters are very similar in these two cases

$$kspr + kppr \simeq 10^{10}(10.2 + 7.2) \exp(-1000 + 680/2RT)$$

$$\simeq 17.4 \times 10^{10} \exp(-840/RT)$$

This approximation is accurate to better than $\pm$ 0.01 x 10^{10} over the range of

temp. used here.

Thus the equation of the line x is

$$\text{Log}\ \frac{k_{Tpr}}{k_2} = (E_2 - 840)/2.303\ RT + \text{Log}\ \frac{10^{10} \times 17.4}{A_2}$$

$$\text{The gradient of the line} = \frac{E_2 - 840}{4.57} = -\frac{0.076 \times 10^3}{1.36}$$

$$\text{thus}\quad E_2 = -256 + 840 = 584\ \text{cals mole}^{-1}$$

$$\text{and}\quad A_2 = 3.72 \times 10^{10}\ \text{litre moles}^{-1}\ \text{sec}^{-1}$$

These parameters are more like the values expected for ethylene and is is considered that the previous interpretation on the basis of a significant heterogeneous reaction was incorrect, for this system.

At 308°K the above parameters give $\text{Log}_{10} k_2 = 10.16$ and this is in agreement with the value reported recently by Martens [106] who found Log k_2 was constant at 10.2 ± 0.1 between 310° and 400°K. Our value of 10.26 at 400°K is also within his quoted error limits although he implies that Log $A_2 = 10.2 \pm 0.1$ and $E_2 = 0$. He employed a competitive technique using either methyl chloride or ethane as competitor but he states that no evidence for wall effects was obtained. If taken literally this latter claim is extremely dubious as it disagrees not only with the results of this thesis, but also with a large number of other published papers (see 1.5). However it is quite possible that an aged RV would be of similar activity to that of the UF coated vessel used here, in which case wall effects would be negligible relative to a photolytic reaction, but care would still have to be taken not to allow the reactants to stand in the dark, for long, before photolysis.

The 'Arrhenius' graph. (TABLE 5.6)

Chlorine pressure = 25.0 mm.

Run	Reactants in mm. C_3H_8	C_2H_4	Products sPrCl	pPrCl	Multiple pr	Total pr	DCE	Temp. °K
A 1a	227.0	426	294	214	262	770	530	294
b	79.2	148	386	267	230	883	482	"
c	187.6	351	382	273	218	873	522	"
2a	166.7	313.5	303	296	258	857	474	334
b	69.5	129.5	300	283	220	803	394	"
c	139.2	260.5	351	332	196	879	484	"
3a	118	220.7	451	303	224	978	593	308
b	96	180.5	400	285	188	873	486	"
4a	168.3	314.7	297	244	163	704	362	350
b	182	340.7	297	276	145	718	332	"
c	135	252.6	455	374	182	1011	425	"
d	133.2	246.2	362	297	172	831	414	"
5a	133.8	251.5	322	292	233	847	445	314
b	179.6	334.8	306	300	197	803	434	"
6a	146	275	306	303	158	767	256	374
b	252.3	471.5	312	250	156	718	282	"
c	123	230	332	297	224	853	259	"
7a	209.4	393.5	335	316	162	813	194	408
b	110	206.5	359	333	171	863	178	"
c	106.4	199.7	300	286	134	720	177	"
8a	166.6	314.2	356	354	133	843	162	425
b	102.6	192.7	347	324	149	820	165	"
9a	140.5	263	157	213	0	370	62	457
b	126.1	237	98	118	0	216	104	"

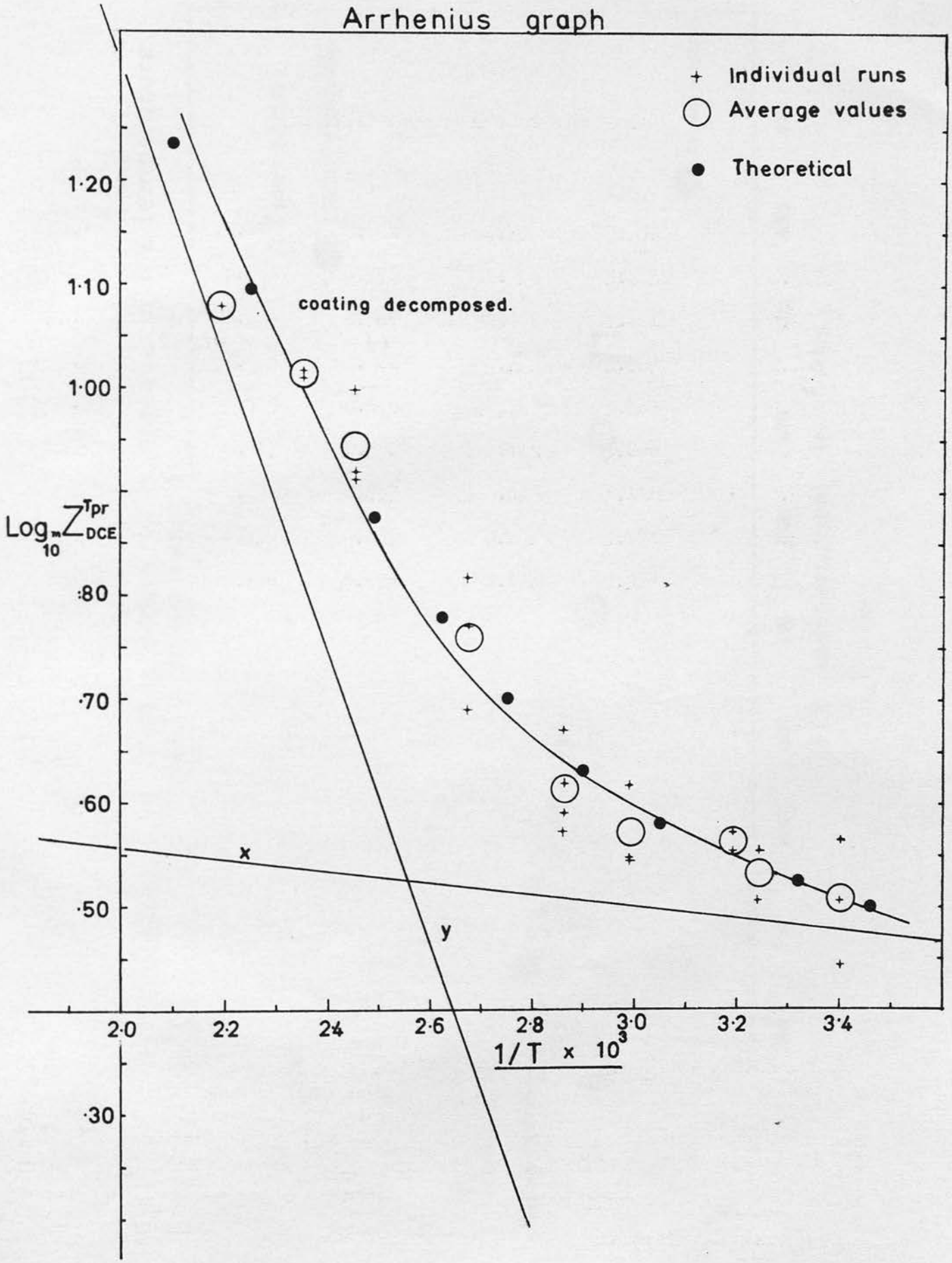
$\frac{1}{T} \times 10^3$	Z_{DCE}^{Tpr}	$Log_{10} Z_{DCE}^{Tpr}$		Total Products		Calculated (see text)
3.40	2.793	0.446		1300		
"	3.690	0.567	0.507	1365	1353	1353
"	3.266	0.509		1395		
2.99	3.521	0.547		1331		
"	4.167	0.620	0.572	1197	1297	1192
"	3.546	0.550		1363		
3.24	3.226	0.509	0.532	1571	1465	1306
"	3.597	0.556		1359		
2.86	3.759	0.575		1066		
"	4.167	0.620	0.615	1050	1199	1138
"	4.695	0.672		1436		
"	3.906	0.592		1245		
3.19	3.745	0.574	0.564	1392	1314	1268
"	3.584	0.554		1237		
2.67	5.952	0.775		1023		
"	4.902	0.690	0.761	1000	1045	1063
"	6.579	0.818		1112		
2.45	8.197	0.914		1007		
"	10.000	1.000	0.945	1041	982	976
"	8.333	0.921		897		
2.35	10.420	1.018	1.015	1005	995	938
"	10.26	1.011		985		
2.19	12.05	1.081	1.081	432	432	870
"	4.115	0.614		320	Coating decomposed.	

TABLE 5.7

'Best fit' for experimental curve.

$10^3 \times \frac{1}{T}$	$\text{Log}_{10}\, k_y$	$\text{Log}_{10}\, k_x$	k_y	k_x	$\text{Log}_{10}(k_y + k_x)$
2.1	1.170	0.551	14.79	3.556	1.264
2.25	0.956	0.542	9.036	3.483	1.097
2.49	0.620	0.529	4.169	3.381	0.878
2.62	0.436	0.522	2.729	3.327	0.782
2.75	0.255	0.514	1.799	3.266	0.705
2.90	0.047	0.506	1.114	3.206	0.636
3.05	- 0.161	0.497	0.690	3.141	0.583
3.32	- 0.530	0.483	0.295	3.041	0.526
3.46	- 0.726	0.475	0.188	2.985	0.501

Fig 5.7


Arrhenius graph
+ Individual runs
Average values
Theoretical
coating decomposed.
1·20
1·10
1·00
·80
·70
·60
·50
·30
$\log_{10} Z^{Tpr}_{DCE}$
x
y
2·0
2·2
2·4
2·6
2·8
3·0
3·2
3·4
1/T x 10^3

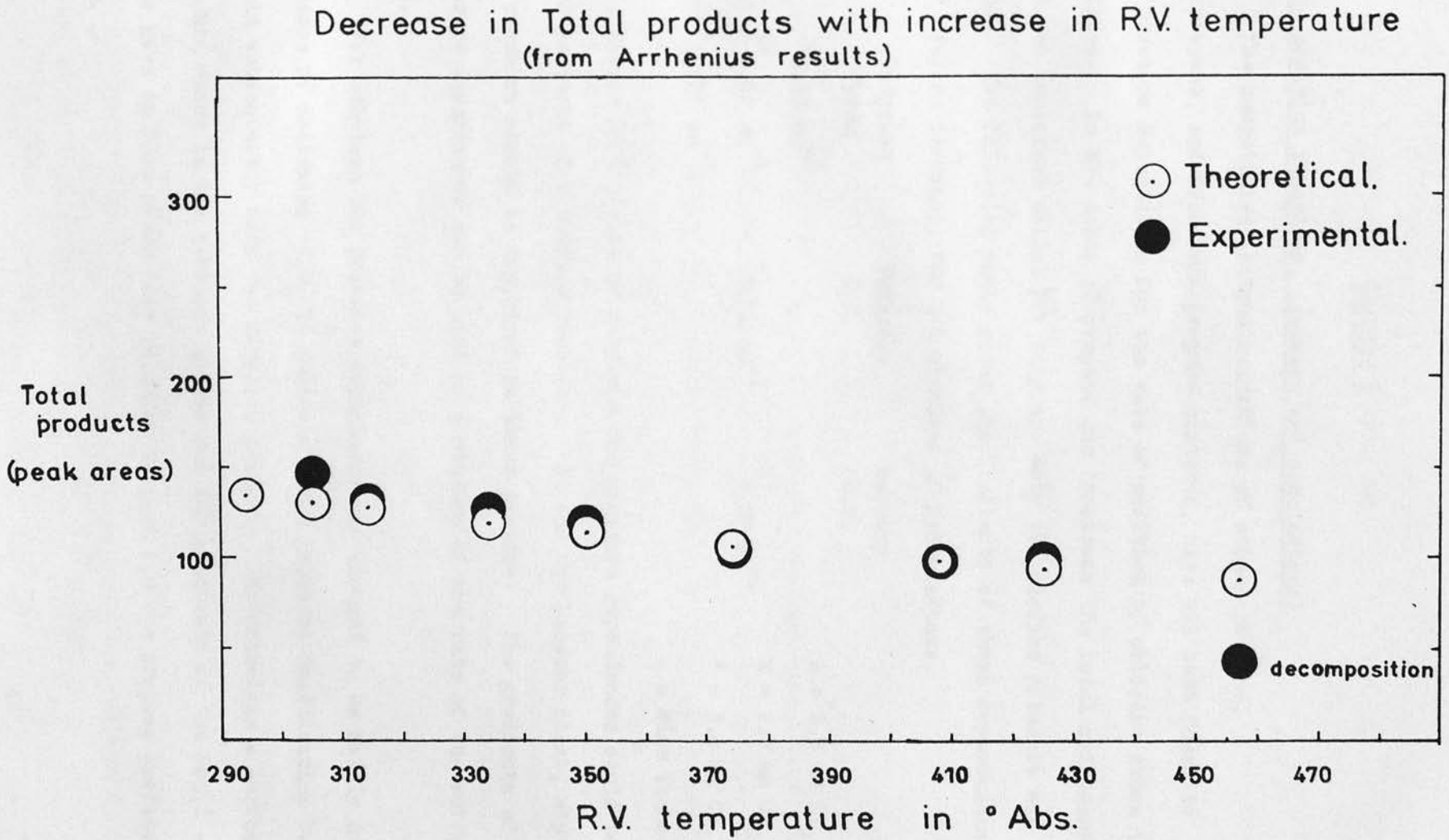

Decrease in Total products with increase in R.V. temperature
(from Arrhenius results)
Theoretical.
Experimental.
decomposition
Total products (peak areas)
300
200
100
290
310
330
350
370
390
410
430
450
470
R.V. temperature in ° Abs.

Fig 5.8

CHAPTER 6

6.1 The addition reactions, (summary and conclusions)

The competitive photochlorinations of ethene:propane, propene:propane, and isobutene:propane mixtures, have all been found to exhibit pressure dependences for the rate of addition of chlorine atoms to the olefines. In the cases of propene and isobutene the total hydrocarbon pressure was important whilst for ethylene only the olefine pressure was important. The following table gives the gradients of these dependences in terms of olefine pressure, for 1/1 mixtures of hydrocarbons.

Lamp	Tungsten	Tungsten	Mercury	
	RV	Pyrex	U.F.	U.F.	
C_4H_8	$^{o}1.52\ cm^{-1}$	-	-	o = 1.5 mm Cl_2
C_3H_6	$^{+x}0.42\ cm^{-1}$	$^{*}0.54\ cm^{-1}$	$^{*}0.27\ cm^{-1}$	x = 2.0 mm Cl_2
C_2H_4	$^{o}(0.07\ cm^{-1})$			* = 3.0 mm Cl_2
				+ = Miss Thomson

Except in the case of ethylene the pressure dependences could be explained in terms of a surface reaction. It was not however clear, why the propane pressure should be important in these systems. The gradients of these two pressure dependences can be used as a measure of the rate of the surface reaction.

For ethylene the pressure dependence was thought to be mainly due to the presence of activated $\cdot C_2H_4Cl^{*}$ radicals which required deactivation before they could subsequently form the dichloro product. Nevertheless a surface reaction did occur in the ethylene system and the gradients of the $\text{Log}(1 + R)$ v t_d graphs gave an idea of its rate relative to that for the propene surface reaction.

Lamp RV	Tungsten Pyrex	Tungsten U.F.	Mercury U.F.
	$10^4 \times k_d$ min^{-1}	$10^4 \times k_d$ min^{-1}	$10^4 \times k_d$ min^{-1}
C_3H_6	82	63	-
C_2H_4	-	-	1.95

If it is assumed that changes in surface and light intensity produce the same proportional changes in rate for all three surface reactions then a combination of the above tables gives the relative rates of the surface reactions as:-

C_2H_4	C_3H_6	C_4H_8
1	16	61

For isobutene and propene the surface reactions were significant relative to the photolytic reactions, and to obtain the rate constant for the photolytic reaction it was necessary to extrapolate to zero 'dark' rate.

In contrast, for ethylene, particularly in a U.F. coated vessel the 'dark' rate was negligible but the activated radical effect and the decomposition of the urea resin at high temperatures caused further complications. The rate constants found for the photolytic addition reactions at 308°K were as follows:-

	C_2H_4	C_3H_6	C_4H_8
Log k_2	10.16	10.20 ± 0.1	10.62 ± 0.2

The error limits quoted have been estimated from the reliability of the intercepts at zero olefine pressure. It is more difficult to estimate the error for ethylene in view of the method of interpretation used, but a somewhat arbitrary estimate may be made by judging the likely extreme positions of the line in Fig 5.7. This gives:-

$$\text{Log } k_2 = 10.6 \pm 0.3 - (584 \pm 540/2.303\ RT)$$

and Log $k_2 = 10.16 \pm 0.1$ at 308°K

Future work

The effect of CO_2 on the ethylene system was not sufficiently investigated here, and it is possible that high pressures of an inert gas of this sort would help to deactivate the $C_2H_4\overset{*}{C}l$ radical. In fact high CO_2/olefine ratios might also have beneficial effects on the propene and isobutene systems, by reducing the amount of olefine adsorbed on the surface. An increase in temperature might also be advantageous in these latter systems for the same reason.

It is probable that surface reactions play a much more important role in so called 'gas' kinetics, than is generally acknowledged and it is advisable that all such kinetic studies should incorporate a detailed check on the absence or presence of significant heterogeneous processes.

Note. Some of the work presented here has been published and the inside back cover holds an off-print of the paper. The results given in the paper have been adjusted in this thesis by the application of analytical calibration factors.

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Appendix A.

General Reaction Mechanisms

RH = alkane A = olefine X_2 = halogen

Initiation

$X_2 + M = 2X\cdot + M$ (1) Thermal

$X_2 + h\nu = 2X\cdot$ (1) Photochemical

Propagation

$X\cdot + RH = XH + R\cdot$ (2') $X\cdot + A = \cdot AX$ (2)

$R\cdot + X_2 = RX + X\cdot$ (3') $\cdot AX + X_2 = AX_2 + X\cdot$ (3)

Inhibition

$R^\bullet + XH = RH + X\cdot$ (-2') $\cdot AX = A + X\cdot$ (-2)

$X^\bullet + RX = X_2 + R\bullet$ (-3') $X^\bullet + AX^\bullet_2 = X_2 + AX$ (-3)

Termination

$R^\bullet + R = R_2$ (4') $\bullet AX + \bullet AX = (AX)_2$ (4)

$R\bullet + X = RX$ (5') $\bullet AX + \bullet X = AX_2$ (5)

$X\cdot + X\cdot + M = X_2 + M$ (6)

Molecular

$RH + X_2 = RX + XH$ (9') $A + X_2 = AX_2$ (9)

$RX + XH = RH + X_2$ (10')

The hydrogen scheme is the same as that for alkanes except for the termination steps (4') and (5') which become:-

$H^\bullet + H^\bullet + M = H_2 + M$ (4")

$X^\bullet + H^\bullet + M = HX + M$ (5")

also the following termination steps have been postulated for the reaction with chlorine

$Cl^\bullet + Y = ClY$ (7')

$H^\bullet + Y = HY$ (8')

Appendix B

Proof to show that the equation

$$\frac{k_2}{k_2'} = \frac{(\Delta RH)(A)m}{(\Delta A)(RH)m}$$

is accurate for up to 30% consumption of both RH and A.

In deriving this equation the approximations made were that,

$$\text{Ln}\left[1 + \frac{(\Delta A)}{(A)f}\right] = \frac{(\Delta A)}{(A)m} \quad \text{and likewise} \quad \text{Ln}\left[1 + \frac{(\Delta RH)}{(RH)f}\right] = \frac{(\Delta RH)}{(RH)m} .$$

It is therefore necessary to prove that these approximations will introduce only a small % error, even when consumption is 30%.

$$\text{By expansion} \quad \text{Ln}\left[1 + \frac{(\Delta A)}{(A)f}\right] = \frac{(\Delta A)}{(A)f} - \frac{(\Delta A)^2}{2(A)^2f} + \frac{(\Delta A)^3}{3(A)^3f} + \ldots\ldots\ldots\ldots$$

$$\text{Now} \quad (A)f = (A)m - \tfrac{1}{2}(\Delta A) = (A)m\left[1 - \frac{(\Delta A)}{2(A)m}\right]$$

$$\text{Let} \quad (\Delta A)/(A)m = X$$

$$\text{Then} \quad \text{Ln}\left[1 + \frac{(\Delta A)}{(A)f}\right] = X(1 - \tfrac{1}{2}X)^{-1} - \tfrac{1}{2}X^2(1 - \tfrac{1}{2}X)^{-2} + \tfrac{1}{3}X^3(1 - \tfrac{1}{2}X)^{-3}\ldots\ldots$$

$$= X(1 + \tfrac{1}{2}X + \tfrac{1}{4}X^2 + \ldots) - \tfrac{1}{2}X^2(1 + X + \ldots) + \tfrac{1}{3}X^3(1 + \ldots\ldots)$$

Collecting terms up to cubic powers

$$= X - X^3(\tfrac{1}{4} - \tfrac{1}{2} + \tfrac{1}{3})$$

$$= X - \tfrac{1}{12}X^3 \quad = X(1 - \tfrac{1}{12}X^2)$$

Thus the error introduced by this method, to the first approximation

$$= \tfrac{1}{12}X^2$$

For an error of 1% $\quad \tfrac{1}{12}X^2 = 0.01 = \tfrac{1}{12}\,(\Delta A)^2/(A)^2m$

Therefore $\quad (\Delta A)/(A)m = 0.35$

continued on next page

Appendix B contd.

$$\text{that is} \quad (A)i - (A)f = 0.35 \times \tfrac{1}{2}\left[(A)i + (A)f\right]$$

$$\text{i.e.} \quad (A)f = 1.65/2.35 \times (A)i$$

$$= 0.7\ (A)i$$

Thus this approximation is accurate to 1% provided the consumption of olefine is less than 30%.

An exactly similar proof applies to the approximation for $\text{Ln}\left[1 + (\Delta RH)/(RH)f\right]$

Thus the ratio

$$\frac{(\Delta RH)}{(RH)m} \times \frac{(\Delta A)}{(A)m}$$

is accurate to $\pm 2\%$ provided the consumptions of both olefine and alkane are less than 30%.

Appendix C

Specimen Calculations

Run 3 $t_d 5$ Reactants:- 69mm C_2H_4, 31.4mm C_3H_8, 10mm Cl_2.

Analytical Results

sprCl	pprCl	Multiple pr	Total pr	1.2 DCE
187	142	122	451	191

Log $(1 + R')$.

$$\text{Log}(1 + R') = \text{Log}(1 + \frac{191}{451}) = 0.153$$

$i Z^{DCE}_{Tpr}$

$$i Z^{DCE}_{Tpr} = \frac{(DCE)(C_3H_8)\text{initial}}{(\text{Total pr})(C_2H_4)\text{initial}} = \frac{191 \times 31.4}{451 \times 69} = 0.192$$

$m Z^{DCE}_{Tpr}$

$$m Z^{DCE}_{Tpr} = \frac{(DCE)(C_3H_8)\text{ mean}}{(\text{Total pr})(C_2H_4)\text{ mean}}$$

$$\text{Now } (C_3H_8)\text{ mean} = (C_3H_8)_i - \tfrac{1}{2}(\Delta C_3H_8)$$

$$\text{and sim. } (C_2H_4)\text{ mean} = (C_2H_4)_i - \tfrac{1}{2}(\Delta C_2H_4)$$

$$\text{Propane consumed} = (\Delta C_3H_8) = (Cl_2)\frac{(\text{Total pr})}{(\text{Total pr}) + (DCE)}$$

$$\text{and sim. } (\Delta C_2H_4) = (Cl_2)\frac{(DCE)}{(DCE) + (\text{Total pr})}$$

$$\text{Thus } (\Delta C_3H_8) = 10 \times 451/(451 + 191) = 7.04 \text{ mm.}$$

$$\text{therefore } (C_3H_8)_m = 31.4 - 3.52 = 27.88 \text{ mm.}$$

$$\text{similarly } (C_2H_4)_m = 69 - 1.49 = 67.51 \text{ mm.}$$

$$\text{hence } m Z^{DCE}_{Tpr} = 0.175$$

Bull. Soc. Chim. Belg., **71**, pp. 764-771, 4 fig. (1962)

THE COMPETITIVE CHLORINATION OF PROPANE AND OLEFINS

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SUMMARY

By chlorinating mixtures of propane and olefins (ethylene, propene and isobutene) we have shown that there is a strong heterogeneous component in the chlorination of the olefins. The heterogeneous reaction can be somewhat reduced by choosing a suitable reaction vessel surface but cannot be completely eliminated. However in favourable cases it can be allowed for and the ratios of the rate constants for chlorine atom attack on propane and olefins can be determined. The absolute rate constants for addition of chlorine atoms to olefins can then be derived using the known value of the rate constant for $Cl + C_3H_8 = C_3H_7 + HCl$.

The competitive method of studying chlorination reactions has been used successfully to determine the absolute rate constants for chlorine atom abstraction reactions (reaction 2) ([1-6]). It was the aim of the present work to determine the rate constants for addition of chlorine atoms to simple olefins by competitive chlorination of olefins and propane, k_2 being known for propane ([3]). The expected reactions in a competition between a hydrocarbon RH, an olefin A and chlorine atoms when the ACl radical is stable (i.e. below about 150°C) ([7]) are :

$$Cl + RH = R + HCl \qquad (2)$$
$$R + Cl_2 = RCl + Cl \qquad (3)$$
$$Cl + A = ACl \qquad (2')$$
$$ACl + Cl_2 = ACl_2 + Cl\,. \qquad (3')$$

To a good approximation when the percentage consumptions of A and RH differ by less than 30% the rate constant ratio $k_{2'}/k_2 = R$, where R is the concentration ratio

$$R = [ACl_2]\,[RH]_m/[RCl]\,[A]_m$$

$[ACl_2]$ and [RCl] are the yields of the two chloride products which we determine by gas chromatography, and $[RH]_m$ and $[A]_m$ are the mean concentrations of hydrocarbon and olefin during the reaction.

An essential test of the simple mechanism is that the concentration ratio R is independent of the concentration of hydrocarbon, chlorine or any additive which does not react with R or ACl. If R does depend upon any of these factors the mechanism is more complex than supposed and $R \neq k_2'/k_2$.

Experimental

Experiments were carried out in a 50 ml Pyrex reaction vessel which was thermostatted at 35°C. The reaction vessel was illuminated when desired by light from a 250 w tungsten filament projection lamp placed about 20 cm from the reaction vessel. The light was filtered and roughly focussed by means of a spherical 1 litre flask containing copper sulphate solution. When the reaction vessel was not illuminated it could be kept in complete darkness by a light tight jacket. The rest of the high vacuum apparatus was of conventional design except that all taps which came in contact with chlorine or the reaction products were metal valves with teflon seats and glands (manufactured by F.J. Hone Ltd., 19 Eldon Park, London S.E. 25). Solution of reactants and products in tap grease was thereby avoided.

Reaction products were analysed by gas chromatography using hydrogen as carrier gas and a katharometer as detector.

Reactants were taken from cylinders and purified by trap to trap distillation. They were degassed under high vacuum. The purity thus attained was certainly not sufficient for overall kinetic studies and it is likely that the reaction chains were terminated by first order removal of free radicals.

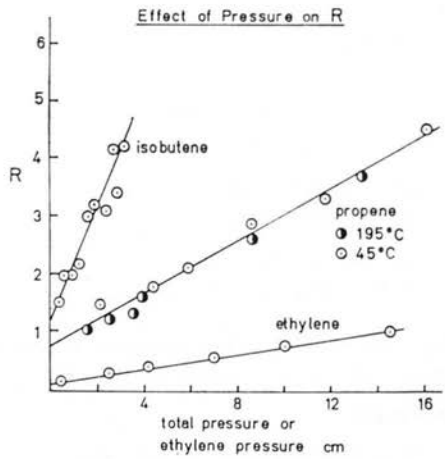

Fig. 1 — The effect of hydrocarbon pressure on the parameter R for mixtures of propane with ethylene, propene and isobutene at 35°C (except for propene/propane mixtures). Chlorine pressure = 1.5 mm Hg. Surface = clean Pyrex.

Results

Figures 1 and 2 show that the ratio R is not independent of hydrocarbon concentration as required by the simple mechanism : R increases linearly with total hydrocarbon pressure for propene/propane and isobutene/propane mixtures and linearly with ethylene pressure (propane pressure has no influence) for ethylene/propane mixtures.

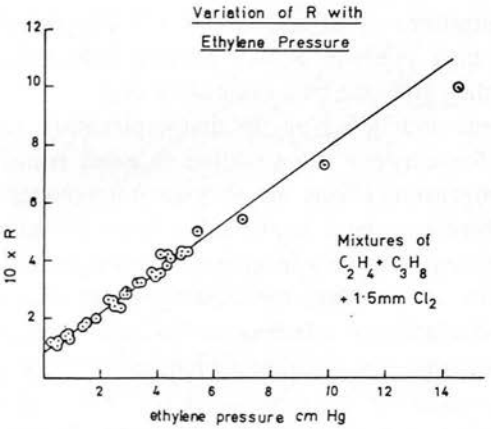

Fig. 2 — The effect of ethylene pressure on the parameter R for ethylene/propane mixtures at 35°C. Chlorine pressure = 1.5 mm Hg. Composition varied from 1/1 to 10/1. Surface = clean Pyrex.

There are two reasonable explanations for this behaviour :

1) The chlorination of the olefin may be partly heterogeneous, the heterogeneous reaction having a higher order than the homogeneous free radical chlorination.

2) If the chlorination of the olefin is homogeneous the dependence of R upon hydrocarbon concentration can be explained by supposing that the ACl radical is initially formed in an activated state as proposed by Ayscough, Cocker and Dainton ([8]). The ACl* then decomposes into A + Cl unless deactivated by collision. Reaction (2′) must then be replaced by four reactions :

$$\begin{aligned} A + Cl &= ACl^* && (2'') \\ ACl^* &= A + Cl && (a) \\ ACl^* + Cl_2 &= ACl + Cl_2 & & \\ \text{or} \quad & ACl_2 + Cl && (c) \\ ACl^* + M &= ACl + M && (d) \end{aligned}$$

where M represents any molecule other than Cl_2 which can deactivate the ACl* radicals. The olefin itself would be expected to be the most potent deactivator but deactivation by other molecules might be observable if this scheme held. The ratio R is now given by the more complex expression

$$R = \frac{k_2''}{k_2} \cdot \left(\frac{k_c[Cl_2] + k_d[M]}{k_a + k_c[Cl_2] + k_d[M]} \right)$$

At low concentrations of M and Cl_2, R will be proportional to [M]; at sufficiently high pressure R will become independent of reactant pressures and then gives the true value of k_2''/k_2.

For propene and isobutene the first explanation accounts for the observations: for ethylene the situation is more complex. There are certainly heterogeneous effects but they cannot account for the observations and there may be a contribution from an activated molecule scheme. Experiments are now in progress to test this hypothesis.

Experiments to elucidate the heterogeneous effects were carried out with propene/propane mixtures at 35°C in Pyrex reaction vessels with various coatings. In order to eliminate any dark reaction which might occur outside the reaction vessel the following procedure was adopted. Chlorine at a pressure of a few mm Hg was added to the evacuated reaction vessel in the dark. This was followed by 5-10 cm of a roughly equimolar propene/propane mixture. The reaction was allowed to proceed in the dark for a measured time. The remaining molecular chlorine was then destroyed by illuminating the mixture for 30 mins. If the dark reaction is assumed to be first order in chlorine and to produce only 1,2 dichloropropane, the rate of formations of dichloropropane during the dark period may be written Rate $= k_{het}[Cl_2]$ where k_{het} may depend upon both the hydrocarbon pressure and the nature of the surface. It can then be readily shown that

$$\ln (1 + R') = \ln (1 + R_0') + k_{het} t_d$$

where t_d is the duration of the dark period, R′ is the ratio $[ACl_2]/[RCl]$ at the end of the experiment, and R_o' the ratio of chloride products which would be obtained if there were no period of dark reaction. Figures 3-5 show that plots of $\ln (1 + R')$ against t_d are indeed straight lines as predicted.

Figure 3 shows plots of $\log_{10}(1 + R')$ against t_d for a number of reaction vessel surfaces. The rate of the dark reaction varies widely with the nature of the surface but it cannot be reduced to zero. It is

therefore possible that some homogeneous dark reaction occurs. In subsequent work a urea-formaldehyde resin surface prepared in situ was used since it had low activity and gave reproducible results.

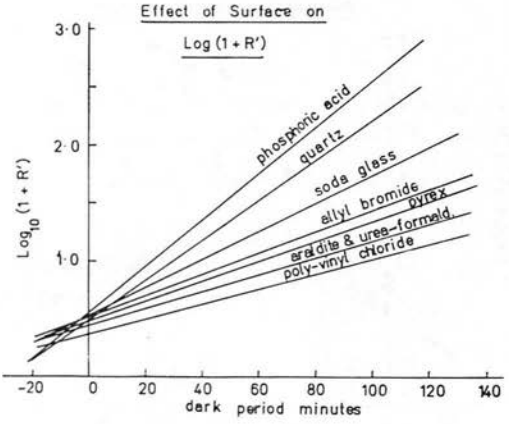

Fig. 3 — The effect of surface on the dark reaction at 35°C for propene/propane mixtures. Approximate mixture composition : 15 mm Hg propane, 15 mm Hg propene, 1.5 mm Hg chlorine.

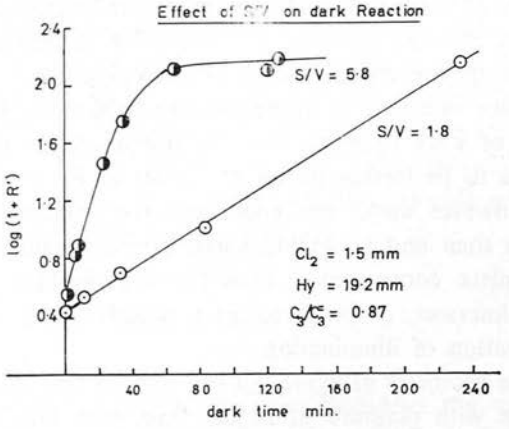

Fig. 4 — The effect of surface/volume ratio on the dark reaction at 35°C for propene/propane mixtures. Surface = urea formaldehyde resin.

The effect of change in surface to volume ratio is shown in figure 4. The effect is what might be expected for a heterogeneous reaction and there is no evidence for any homogeneous dark reaction. The flattening

of the curve for the packed reaction vessel at values of Log (1 + R′) above 2.2 may be explained by a slight light leak into the reaction vessel or by a very slow heterogeneous chlorination of propane.

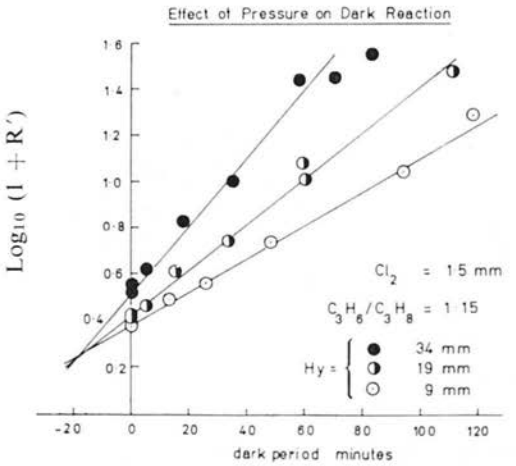

Fig. 5 — The effect of hydrocarbon pressure on dark reaction at 35°C for propene/propane mixtures. Surface = urea formaldehyde resin.

The effect of change of total pressure on the heterogeneous reaction at a constant chlorine pressure of 1.5 mm Hg is shown in figure 5. k_{het} increases approximately linearly with total hydrocarbon pressure. The three lines intersect at approximately −20 mins. Had the light source been of such intensity that the homogeneous reaction could be considered to be instantaneous, all values of R_o' should have been the same. However under our conditions the homogeneous reaction took a finite time and inevitably some heterogeneous reaction must have taken place concurrently. Thus the lines in figure 5 would be expected to intersect, as observed, at a negative time somewhat less than the duration of illumination.

From the geometry of figure 5 it can be seen that the intercepts R_o' must increase with pressure. It is just from such intercepts that the ratio R (plotted in figure 1) is calculated.

It seems that for propene/propane mixtures the increase in R with pressure can be adequately explained by the occurrence of concurrent heterogeneous and homogeneous reactions. The rate of the heterogeneous reaction decreases with pressure of hydrocarbon and it is likely that at very low pressures of hydrocarbon its rate will be negligible. Thus

the intercept of lines in figures 1 and 2 on the y axis will give the true value of k_2'/k_2. Likewise the intersection of the three lines in figure 5 should give the same value. The values of k_2' obtained in this way for propene, making use of the known value of k_2 for propane, is given in the table.

TABLE 1

Rate constants for addition of Cl *to olefins*

Olefin	Temperature	$\text{Log}_{10}k_2'$ (1)	Reference
C_2Cl_4	110-210°C	9.20	5,4.
$C_2H_2Cl_2$	30-65°C	9.43	9
sec C_3H_8	35°C	10.36	3
C_2H_4(2)	35°C	9.3 ± 0.1	this work
C_3H_6	35°C	$10.2_5 \pm 0.1$	this work
iC_4H_8	35°C	10.4 ± 0.1	this work

(1) The units of k are $1.\text{mole}^{-1}\,\text{sec}^{-1}$.
(2) See text for discussion of reliability of value of k_2'.

The results obtained with isobutene, although less extensive, are similar and indicate that the reaction has a strong heterogeneous component. The rate of this reaction is so high that considerable difficulty was experienced in obtaining reproducible results. The heterogeneous chlorination of isobutene differs from that of propene in that it produces $CH_2Cl.C(CH_3)=CH_2$ in amounts comparable with the yield of dichloroisobutane. Only very small quantities of allyl chloride are formed in the heterogeneous chlorination of propene.

Conclusions

We believe that with propene and isobutene the values of the intercepts in figure 1 and of the intersection of lines in figure 5 can be used to calculate true values of k_2'/k_2 and hence absolute values of k_2'.

For ethylene the intercept in figure 2 appears to give too low a value for k_2'. The value obtained is an order of magnitude lower than that for propene or isobutene; it is approximately equal to the value obtained for C_2Cl_4 by Goldfinger et al (5) and somewhat lower than

that obtained by Ayscough et al. ([9]) for cis-dichloroethylene. Rough transition state calculations similar to those previously carried out for alkanes ([10]) indicate that the A factor for Cl atom attachment to ethylene should be five to ten times that for attachment to chlorinated ethylenes containing two or more Cl atoms. Since the activation energy for $Cl + C_2H_4$ is not likely to be greater than that for $Cl + C_2Cl_4$ it is probable that the rate constant for the former reaction is at least five times greater than for the latter.

Dr. G. Martens (Brussels) said :

1. We have now been able to measure the rate constant of $C_2H_4 + Cl$; a constant value has been found $\log k_2 = 10.2 \pm 0.1$ between 310 and 400°K competing ethylene either with methyl chloride or with ethane.

2. In both cases the absence of wall effects has been checked by a careful analysis following the reaction order up to approximately 30%. I believe that careful checks of the reaction mechanism, as done in this paper, are of particular interest even if the mechanism is believed to be known.

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